

Methods and Apparatus for Determining Particle Characteristics  
By Measuring Scattered Light

Related Applications

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TECHNICAL FIELD OF THE INVENTION

In general, the present invention relates to systems and methods that analyze particles in a sample using laser light diffraction. More particularly, the present invention relates to systems and methods that analyze laser light diffraction patterns to determine the size and characteristics of particles in a sample.

Dynamic light scattering has been used to measure particle size by sensing the Brownian motion of particles. Since the Brownian motion velocities are higher for smaller particles, the Doppler broadening of the scattered light is size dependent. Both heterodyne and homodyne methods have been employed to create interference between light scattered from each particle and either the incident light beam (heterodyne) or light scattered from the other particles (homodyne) of the particle ensemble. Heterodyne detection provides much higher signal to noise due to the mixing of the scattered light with the high intensity light, from the source which illuminates the particles, onto a detector. Usually either the power spectrum or the autocorrelation function of the detector current is measured to determine the particle size. These functions are inverted using algorithms such as iterative deconvolution to determine the particle size distribution. This document describes concepts which use a beamsplitter and a mirror or partial reflector to mix the light from the source with light scattered by the particles. This document also describes concepts which use a fiber optic coupler to mix the light from the source with light scattered by the particles.

In Figure 1 a light source is focused through a pinhole by lens 1 to remove spatial defects in the source beam. The focused beam is recollimated by lens 2 which projects the beam through an appropriate beamsplitter (plate, cube, etc.). The diverging light source, lens 1, pinhole 1, and lens 2 could all be replaced by an approximately collimated beam, as produced by certain lasers. This nearly collimated beam is focused by lens 3 into the particle dispersion which is contained in a sample cell or container with a window to pass the beam. The focused beam illuminates particles in the dispersion and light scattered by the particles passes back through the window and lens 3 to be reflected by the beamsplitter through lens 4 and pinhole 2 to a detector. A portion of the incident collimated source beam is reflected from the beamsplitter towards a mirror, which reflects the source light back through the beamsplitter and through the same lens 4 and pinhole 2 to be mixed with the scattered light on the detector. This source light provides the local oscillator for heterodyne detection of the scattered light from the particles. The mirror position must be adjusted to match (to within the coherence length of the source) the optical pathlengths traveled by the source light and the scattered light. This is accomplished by approximately matching the optical path length from the beam splitter to the scattering particles and from the beam splitter to the mirror. The interference between scattered and source light indicates the velocity and size of the particles. The visibility of this interference is maintained by pinhole 2 which improves the spatial coherence on the detector. Pinhole 2 and the aperture of lens 3 restrict the range of scattering angle (the angle between the incident beam and the scattered light direction) to an angular range around 180 degrees.

Multiple scattering produces errors in the power spectrum or autocorrelation function of the detector current. Multiple scattering can be reduced by moving the focus of lens 3 to be close to the inner surface (the interface of the dispersion and the window) of the sample cell window. Then each scattered ray will encounter very few other particles before reaching the inner window surface. Particles far from the window will show multiple scattering, but they will contribute less to the

scattered light because pinhole 2 restricts the acceptance aperture, which will capture a smaller solid angle of scattered light from particles which are far from the inner window surface. If the sample cell is a removable cuvette, multiple scattering will be reduced as long as the short distance of inner window surface to the focal point (in the dispersion) of lens 3 is maintained by appropriate position registration of the cuvette.

This design can provide very high numerical aperture at the sample cell, which improves signal to noise, reduces multiple scattering, and reduces Mie resonances in the scattering function. Light polarization is also preserved, maximizing the interference visibility.

Figure 2 shows another version of this concept where lower scattering angles are measured by separating the incident and scattered beams. Mie resonances are reduced at lower scattering angles. Also multiple scattering is reduced by eliminating the scattering contribution of particles far from the lens 3 focus in the particle dispersion. Only particles in the volume of the intersection of the incident light cone and scattered light cone, defined by the image of the pinhole 2 in the sample cell, contribute to scattering passing through pinhole 2. If this volume is close to the inner wall of the sample cell window, all scattered rays will have a very short transit through the particle dispersion, with minimal multiple scattering. The sample cell window should be tilted slightly so that the Fresnel reflection of the incident beam from the window surface does not enter pinhole 2 though the aperture on lens 4. However if this reflection were large enough, the window surface reflected light could provide the local oscillator for heterodyne detection, without the need for the mirror by providing the proper window tilt to pass the window reflection through the lens 3 aperture and pinhole 2.

Figure 3 shows a similar configuration to Figures 1 and 2, except that the mirror has been replaced by a retro-reflector or corner cube. The alignment of this configuration will be more stable because the retro-reflector reflects light at 180 degrees to the incident beam over a wide range of incident angles.

Figure 4 shows a configuration where the local oscillator is created by a reflection from the coated convex surface of a plano-convex lens (lens 5) or some other partially reflecting convex surface. The center of curvature of this convex surface coincides with the focus of the incident laser beam, from lens 3, in air. This convex surface provides a partially reflecting surface which is normal to the incident rays. Therefore, the reflected light will focus through pinhole 2, along with the scattered light, even though the scattering surface is not coincident with the focus. If the beam focus were focused at the inner surface of the sample cell window, then this planar sample cell window surface could provide the reflection for the local oscillator, without the need for the convex surface. However, then the signal would be sensitive to the motion of the sample cell, requiring stable mechanical registration of the cuvette. Lens 5 can be attached firmly to the structure of the optical system, maintaining the high mechanical stability required by an interferometer. Also the reflectivity of the convex surface is more easily increased by reflective coatings, than the inner surface of the sample cell window. Lens 5 could also be replaced by a plano partially reflecting mirror between the beamsplitter and lens 3. The tilt of this partially reflecting mirror must be adjusted to reflect a portion of source light back through lens 4 and pinhole 2. These configurations could also be used with a fiber optic coupler instead of a beam splitter, with appropriate coupling optics at each port of the coupler.

In some cases, the beam focus will define an interaction volume, in the dispersion, which is too small to contain a statistically significant number of particles. The interaction volume is the volume of the particle dispersion which contributes to the scattered light collected by the optics. In particular, a sample of larger particles at low concentration may not be representative of the total sample if the exchange of particles in and out of interaction volume is slow. In this case a larger interaction volume is required to maintain sufficient particles in the beam. So changing the beam focus size and divergence may be appropriate in some applications. Figures 5 and 6 show the interchange of two lenses, lens 3A and lens 3B, to change the size of the interaction volume in the dispersion. In each case the focus of lens 3A or 3B is placed in the dispersion, with a

position which can be adjusted by moving this lens in any direction. For any position of the lens, the scattered light will pass back through pinhole 2 with the local oscillator reflection from the mirror. The partial reflecting mirror in Figures 5 and 6 could also be replaced by the plano partial reflecting mirror between the beamsplitter and lens 3A or lens 3B, as described previously for Figure 4.

Another aspect of Figures 5 and 6 is the use of a partially reflecting mirror to produce the local oscillator for heterodyne detection and to monitor the laser intensity fluctuations. The source light which passes through the partially reflecting mirror is focused by lens 5 onto detector 2. The signal from detector 2 is used to correct the signal on detector 1 for intensity variations and noise in the light source as described by the inventor in this document. The mirror could also be removed to measure the homodyne (self beating) spectrum of the scattered light from the particles.

Also notice that lens 1 and pinhole 1 have been removed in Figures 5 and 6 to show the configuration without removal of spatial defects in the beam. For example, the source could be a laser diode in these figures. If a low divergence beam from a collimated laser, such as a gas laser, were used, the collimating lens 2 could also be eliminated.

Figure 7 shows a probe version of this invention which can be dipped into the dispersion in a container such as a beaker. Since the particles may settle, the beam is folded by a mirror just before passing through the window. Then the beam is projected into the sample in a direction nearly perpendicular to the direction of gravitational settling so that as particles settle out of the interaction volume, they are replaced by other particles which settle into the volume from above. As shown before, the partially reflecting mirror could be fully reflecting. This mirror could also be eliminated for homodyne detection or replaced by a partially reflecting convex surface placed between lens 3 and the window.

Figure 8 shows another variation where a partially reflecting flat mirror, which produces the local oscillator, is placed in

the collimated portion of the beam between the beamsplitter and lens 3. The tilt of this mirror would be adjusted to send the reflection back through pinhole 2. The partially reflecting local oscillator mirror can be placed in this position (between the beamsplitter and the next optic towards the particle sample) in all configurations in this disclosure, where the light is nearly collimated through the beamsplitter.

Another issue is the shift in the heterodyne spectrum due to convection currents in the sample. This is usually small when the divergence of the beam focus is low and the focus is close to the interface between the dispersion and the window. However, this problem may be reduced by surrounding the interaction volume with a chamber as shown in crosssection drawing in Figure 9. This chamber may be made out of material with high thermal capacity and conductivity to bring the interaction volume to thermal equilibrium. Also the height of the inner chamber wall must be sufficient distance from the interaction volume to prevent the larger particles from settling out of the interaction volume during data collection.

All of these configurations can generate a local oscillator for heterodyne detection using the following methods. In all cases the reflector, which generates the local oscillator, must be held in a stable location relative to the rest of the interferometer:

- 1) partially or totally reflecting mirror at the beam splitter, as shown in Figure 1 and Figure 5
- 2) flat partially reflecting surface close to the focus of the beam in the sample. If this is the inner surface of a removable cuvette, it must have stable mechanical registration to avoid interferometric noise due to motion of the partially reflective surface. This would replace the mirror in item 1.
- 3) A flat partially reflecting flat surface between the beamsplitter and lens 3 could replace the mirror in item 1
- 4) A partially reflective convex surface with center of curvature at the beam focus in air could replace the mirror in item 1.

One of the key advantages of this invention is that the beam focus in the dispersion does not need to be coincident or near to a partially reflecting surface, such as the inner surface of a cuvette. If the inner surface of cuvette is not close to the beam focus in the dispersion, very little of the reflection from that surface will be returned through pinhole 2 to contribute interferometric noise from small motion of that surface. This allows the use of inexpensive cuvettes whose poor tolerances may not accommodate the requirements of the optical interferometry in the systems shown above.

Another advantage of these designs is the ease of alignment. All of the components in each design can be positioned to within standard machining tolerances. Only two components need alignment during manufacture: the pinhole and/or the local oscillator reflector. These systems have the following advantages over fiber optic systems:

- better interferometric efficiency in both polarization and coherence
- more flexibility for choice of scattering angle
- better photometric efficiency
- better control over the local oscillator level
- higher numerical aperture in the scattering volume to reduce multiple scattering and increase scatter signal level
- simple adjustment of scattering volume numerical aperture and position in the sample
- adjustable scattering volume
- lower multiple scattering
- lower cost

In the cases where fiber optic systems may have other advantages (such as electromagnetic immunity when using remote sensing) these designs can be changed to gain some of the advantages which are listed above. The following describes some concepts for fiber optic systems.

### **Fiber optic methods and apparatus**

The basic fiber optic interferometer is illustrated in Figure 10. A light source is focused into port 1 of a fiber optic coupler. This source light is transferred to port 4 and light scattering optics, which focus the light into the particle dispersion and collect light scattered from the particles. This scattered light is transferred back through the fiber optic and coupler to the detector on port 2. If the coupler has a third port, a portion of the source light also continues on to port 3 which may provide a local oscillator with a reflective layer. If the local oscillator is not provided at port 3, a beam dump or anti-reflective layer may be placed onto port 3 to eliminate the reflection which may produce interferometric noise in the fiber optic interferometer. The beam dump could consist of a thick window which is attached to the tip of the fiber with transparent adhesive whose refractive index nearly matches that of the fiber and the window. This will reduce the amount of light which is Fresnel reflected back into the fiber at the fiber tip. The other surface of the window can be anti-reflection coated, and/or be sufficiently far (thick window) from the fiber tip, so that no light, which is reflected from that surface, can enter the fiber.

Figure 11A shows one version of the scatter optics on port 4. A lens or gradient index optic (GRIN) focuses the source light into the particle dispersion in a cuvette through a transparent wall of the cuvette. A partially-reflective layer on the tip of the fiber or on the surface of the GRIN rod, at the fiber/GRIN gap, provides the reflection for the local oscillator light to travel back through port 4 with light scattered by the particles. If the fiber surface is partially reflecting, the GRIN surface could be anti-reflection coated or it could be placed sufficiently far from the fiber to avoid reflections from the GRIN surface back into the fiber. Reflections from both surfaces could produce an optical interferometric signal which may contaminate the heterodyning signal from the scattering particles. The GRIN rod surface, which is closest to the cuvette, could also be anti-reflection coated. The reflected source light and the scattered light, from particles in the cuvette, travel back through the coupler and are combined on the



detector at port 2. The interference between these two light components is indicative of the Brownian motion of the particles and the particle size. Since the local oscillator is generated at the exit surface of port 3 or port 4, as opposed to the cuvette surface, the interference signal is not degraded by small errors in the position of the cuvette surfaces, allowing use of inexpensive disposable cuvettes. The local oscillator is provided by light reflected from either port 3 or port 4 fiber optic (or GRIN rod surface). The reflection is provided by a partially reflective surface close to exit surface of the fiber or a layer on the fiber itself as shown in Figures 14 and 13, respectively. Both of these methods can be used on either port 3 or port 4 to create a reflection for the local oscillator. Since the partially reflecting surface is at the exit of the fiber optic, no optical alignment is required for the scattered light or the local oscillator light.

Figure 11B shows another concept where the reflective layer is placed on the end of GRIN rod 1, which is coated to provide the local oscillator reflection. The GRIN rod pitch is chosen so that this surface is conjugate to the fiber tip. Wide spacing, anti-reflection coating, or index matching can be used in the fiber/GRIN gap to reduce reflection at that surface. This configuration has the advantage that only GRIN rod 1 needs to be coated. So hundreds of GRIN rods could be coated in one evaporation or sputtering operation. GRIN rod 2 then transfers the beam into the cuvette. Conventional lenses could also be used to accomplish this design by replacing each GRIN rod with a lens and placing a planar reflecting surface at the intermediate plane which is optically conjugate to the fiber tip. Object and image planes of an optical system are conjugate to each other.

Figure 11B also shows a conventional lens version of this idea which uses a coated window surface at the intermediate conjugate plane to create the local oscillator reflection.

Placing a reflective layer on the tip of the fiber could require placing the entire fiber optic coupler into a vacuum chamber for evaporated or sputtered coatings. The design shown in Figure 12 shows a fiber tip assembly which is removable from the coupler port. This design allows many fiber tip assemblies to be placed

into the sputtering chamber at one time to reduce coating costs. Only the assembly of male fiber optic connectors #2 and #3, or connector #3 alone, needs to be placed into the vacuum chamber for sputtering a partially reflective layer on the tip of connector #3. Index matching gel is placed in the gap between connectors #1 and #2 to reduce reflected light at these surfaces. The GRIN rod assembly with attached female connector can be removed and replaced with other assemblies containing different types of lenses to change the interaction volume (the volume of the particle dispersion which contributes to the scattered light collected by the optics) in the particle dispersion to control the number of particles viewed by the optics. This can be important when concentrations are low and only a few particles are in the interaction volume, producing poor signal statistics. The GRIN rod could also be replaced by a conventional lens. In either case, the lens focal length and position can be adjusted to change the interaction volume, scattering angle range, and numerical aperture (to control scattering sample depth and multiple scattering).

The male/male connector assembly is easily manufactured by butting two male connectors, back-to-back, through a sleeve and pushing a fiber through the entire assembly. This fiber is potted and end polished in both connectors using standard techniques.

Other types of optical systems could also be attached to this port. An example of a probe attachment for insertion directly into the dispersion is shown in Figure 15. The female connector is part of the probe assembly (Figure 15) and the standard GRIN assembly (Figure 12); so that both of these assemblies can be interchanged onto the same coupler without any optical alignment. The source light exits the probe and enters the particle dispersion approximately perpendicular to gravity so that particles that settle out of the interaction volume are replaced by other particles which settle into the volume from above. In all of these cases, the coupling system which consists of male connectors #2 and #3 can be eliminated if the local oscillator is placed directly onto either the fiber tip at port 3 or the fiber tip of male connector #1. And in both of these assembly designs, the partially reflecting surface, for

producing the local oscillator, can be placed on any surface which is conjugate to the exit tip of the port 4 fiber optic and which is mechanically stable with respect to the port 4 tip. One example of this surface is a flat partial reflector between lenses 2 and 3 in Figure 15, or adding a second lens in Figure 12, between the tip of the fiber optic (in fiber optic connector 3) and the particle dispersion, to create an intermediate plane, which is conjugate to the fiber tip, where the partially reflecting surface is placed. However, some optical alignment may be required in these designs.

Another attachment design could use all anti-reflection coated optics, without the partially reflecting surfaces, to completely eliminate any local oscillator source, for homodyne detection.

Also note that in all of the heterodyne designs with the local oscillator reflector in the scatter sensing arm, the optical path difference between the scatter light path and the local oscillator path (the difference between the optical path length from the local oscillator partial reflector to the detector and the scattering particle to the detector) must be less than the coherence length of the light source to provide sufficient interferometric visibility.

For both the fiber optic and non-fiber optic systems, the local oscillator reflection can be generated at certain surfaces. All other surfaces may be tilted and/or anti-reflection coated so as to contribute minimal interferometric signal on the detector. In both the fiber and non-fiber systems, the source beam is focused within the cuvette (or sample cell). If the focused point is far into in the dispersion (see Figure 16), the local oscillator reflection must be created at another surface (other than the cuvette/dispersion interface) as described above. In any case, a spring could be employed to press the cuvette against a registration surface, as shown in Figure 16, to firmly register and position the cuvette. The spring could also be replaced by a clamping screw to avoid the low frequency mechanical resonances of the spring. The cuvette (and cuvette holder) must be mechanically registered to the optical system for two reasons. If the cuvette surface reflection generates the local oscillator, movement of the surface will create interferometric

noise. Also if the cuvette and/or the particles move relative to the optics due to mechanical vibration, non-Brownian Doppler shifts of the scattered light will be detected and will confound the size determination.

This positional registration is even more critical when the beam focus is at the inner surface of the cuvette (the surface contacting the dispersion) and the reflection from that surface is used to generate the local oscillator (see Figure 17). Then any motion of the cuvette will create interferometric noise in the heterodyne signal. So the cuvette must be pinned against a reference surface as shown in Figure 17, where a spring holds the cuvette against an inner surface of the cuvette holder. The beam focus might be placed close to this inner surface to either provide the local oscillator from that surface or to reduce multiple scattering into the pinhole or fiber optic. If the only reason is to reduce multiple scattering and the local oscillator reflection is produced at another surface (other than the cuvette/dispersion interface), then the incident light beam might approach the cuvette at a non-normal incidence angle (see Figure 18 which is the top view of Figure 17) so that the reflected light from that inner surface cannot pass back through the optical system and through the pinhole or fiber to the detector. All reflected light, except for the local oscillator reflection, should be suppressed to reduce interferometric noise from mechanical vibrations and from laser phase noise, and to reduce reflections back into a laser source to reduce laser noise.

For small particles, the heterodyne signals will be buried in laser source noise. Figure 5, Figure 6, and Figure 7 show detector 1, which measures the heterodyne signal from the particles. In Figure 19, detector 2 is the heterodyne detector. Figure 5, Figure 6, and Figure 7 show an additional detector 2, which measures the intensity of the local oscillator laser noise. Figure 19 also shows additional detectors, detector 1 (the rear facet detector on the laser) and detector 3 (a laser power monitor on port 3 of the fiber coupler). Any of these additional detectors, or any detector which monitors the laser power, can be used to monitor the laser noise. Another possibility is to monitor the light that has passed through the

particle dispersion by placing a detector in the sample cell area. In any event, if we define a heterodyne detector current as  $I_1$  and the laser monitor detector current as  $I_2$  we obtain the following equations which hold for each of the heterodyne detectors.

$$I_1 = \sqrt{R \cdot T \cdot R_m \cdot I_o(t) \cdot I_s(t)} \cdot \cos(F \cdot t + A) + R \cdot T \cdot R_m \cdot I_o$$

$$I_1 = \sqrt{R \cdot T \cdot R_m \cdot I_o(t) \cdot S \cdot R \cdot T \cdot I_o} \cdot \cos(F \cdot t + A) + R \cdot T \cdot R_m \cdot I_o$$

$$I_2 = K \cdot T_m \cdot I_o(t)$$

where:

$I_1$  and  $I_2$  are normalized (detector responsivity = 1).

$\cos(x)$  = cosine of  $x$

$K$  is a constant which describes the ratio of other efficiencies (optical and electrical), between the  $I_1$  and  $I_2$  channels, which are not due to the beamsplitter and partial reflecting mirror.

$R$  and  $T$  are the reflectivity and transmission of the beamsplitter, respectively.

$R_m$  and  $T_m$  are the reflectivity and transmission of the partially reflecting mirror, respectively.

$\sqrt{x}$  = square root of  $x$

$I_o(t)$  is the source beam intensity as function of time  $t$

$F$  is the heterodyne beat frequency at a heterodyne detector due to the motion of the scatterer which produces  $I_s(t)$ . And  $A$  is an arbitrary phase angle for the particular particle.

$I_s(t)$  is the scattered light intensity from the particle:

$I_s(t) = S \cdot R \cdot T \cdot I_o(t)$  where  $S$  is the scattering efficiency for the particle.  $S$  includes the product of the scattered intensity per incident intensity and optical scatter collection efficiency.

The light source intensity will consist of a constant portion  $I_{oc}$  and noise  $n(t)$ :

$$I_o(t) = I_{oc} + n(t)$$

We may then rewrite equations for  $I_1$  and  $I_2$ :

$$I_1 = R \cdot T \cdot \sqrt{S \cdot R_m} \cdot (I_{oc} + n(t)) \cdot \cos(F \cdot t + A) + R \cdot T \cdot R_m \cdot (I_{oc} + n(t))$$

$$I_2 = K \cdot T_m \cdot (I_{oc} + n(t))$$

If we use high pass filters to only accept only the higher frequencies, which contain the size information, we obtain high pass signals for  $I_1$  and  $I_2$ :

$$I_{1hp} = R \cdot T \cdot \sqrt{S \cdot R_m} \cdot I_{oc} \cdot \cos(F \cdot t + A) + R \cdot T \cdot R_m \cdot n(t)$$

$$I_{2hp} = K \cdot T_m \cdot n(t)$$

Where we have assumed that  $n(t)$  is much smaller than  $I_{oc}$ . And also  $n(t)$  is the portion of the laser noise that is passed by the high pass filter bandwidth (see below). In certain situations, these high pass filters are replaced by band pass filters which only pass frequencies carrying particle information.

The laser noise can be removed to produce the pure heterodyne signal,  $I_{diff}$ , through the following relationship:

$$I_{diff} = I_{1hp} - (R \cdot T \cdot R_m) / (K \cdot T_m) \cdot I_{2hp} = R \cdot T \cdot \sqrt{S \cdot R_m} \cdot I_{oc} \cdot \cos(F \cdot t + A)$$

This relationship is realized by high pass filtering of each of the  $I_1$  and  $I_2$  detector currents. One or both of these filtered signals are amplified by programmable amplifiers, whose gains and phase shifts are adjustable. The difference of the two outputs of these amplifiers is generated by a difference circuit or differential amplifier. With no particles in the beam, the gain and phase shift of at least one of the programmable amplifiers is adjusted, under computer or manual control, to minimize the output of the difference circuit (i.e.  $(\text{gain } I_2) \cdot R \cdot T \cdot R_m / (K \cdot T_m) = 1$ ). At this gain, the source intensity noise

component in the heterodyne detector beat signal, with particles present, is removed in the difference signal, which is fed to an analog to digital converter (A/D), for inversion to particle size.

This entire correction could be accomplished in the computer by using a separate A/D for each filtered signal and doing the difference by digital computation inside the computer. The phase and gain adjustments mentioned above, without particles in the beam, could be accomplished digitally. Then the coefficient ratio  $R/K$  can be calculated to be used in the equation for  $I_{diff}$ , using the following equation:

$$R \cdot T \cdot R_m / (K \cdot T_m) = I_{1dc} / I_{2dc}$$

Where  $I_{1dc}$  and  $I_{2dc}$  are the DC offsets of the unfiltered signals  $I_1$  and  $I_2$ , respectively.

If both signals were digitized separately, other correlation techniques could be used to reduce the effects of source intensity noise. In any case, the beamsplitter reflection is adjusted to obtain shot noise limited heterodyne detection, with excess laser noise removed by the difference circuit or difference calculation shown above.

These noise correction techniques can be applied to any heterodyning system by simply adjusting the filtering of currents  $I_1$  and  $I_2$  to pass the signal of interest, while blocking the low frequency component ( $I_{oc}$ ) of  $I_o(t)$ . Excess laser noise and other noise components, which are present in both the heterodyne signal and the light source, can be removed from the signal of interest through this procedure. One application is dynamic light scattering, where the heterodyne signal is contaminated by laser source noise in the optical mixing process. The filters on  $I_1$  and  $I_2$  would be designed to pass the important portion of the Doppler broadened spectrum and to remove the large signal offset due to the local oscillator. Then by using the subtraction equation for  $I_{diff}$ , described previously, the effects of laser noise can be removed from the Doppler spectrum, improving the particle size accuracy. In the case of fiber optic heterodyning systems, the laser monitor

current,  $I_2$ , could be obtained at the exit of the unused output port (port 3 in Figure 19) of the fiber optic coupler which is used to transport the light to and from the particle sample, because this port carries light only from the optical source, without any scattered light.  $I_2$  could also be obtained from the laser detector (for example the rear facet detector on a laser diode as shown by detector 1 in Figure 19). This subtraction for  $I_{diff}$  could be accomplished by the analog difference circuit or by digital subtraction after digitization of both the filtered contaminated heterodyne signal and the filtered source monitor as outlined previously. This procedure could also be accomplished using the unfiltered signals, but with much poorer accuracy due to the large signal offsets.

Using Figure 19 we can describe another version of this correction which simply measures the power spectrum at port 2 (detector 2) and port 3 (detector 3) in Figure 19. The signal at port 1 (detector 1) could also be used in place of the detector 3 signal. Also the signals at port 2 and port 3 in Figure 19 could be replaced by the signals at detector 1 and detector 2, respectively, in Figures 5,6, and 7. Let us define the following measurements:

$P2_{bkg}$  = power spectrum measured at port 2 with clean dispersant (without particles) in the sample region

$P3_{bkg}$  = power spectrum measured at port 3, while  $P2_{bkg}$  is being measured on port 2

$P2_{meas}$  = power spectrum measured at port 2 from the particle dispersion (with particles) in the sample region

$P3_{meas}$  = power spectrum measured at port 3, while  $P2_{meas}$  is being measured on port 2

$I3_{dc}$  = DC offset or constant portion of signal producing  $P3_{meas}$

$I2_{dc}$  = DC offset or constant portion of signal producing  $P2_{meas}$

Then the measured power spectrum,  $P2_{meas}$ , can be corrected for the background power spectrum and the drift in the background



power spectrum by using the following equations, where  $P(f \sim 0)$  is the power spectral density at frequencies close and equal to zero:

$$P_{\text{corrected}} = P_{2\text{meas}} - P_{2\text{bkg}} - ((I_{2\text{dc}}/I_{3\text{dc}})^2) * (P_{3\text{meas}} - P_{3\text{bkg}})$$

or

$$P_{\text{corrected}} = P_{2\text{meas}} - P_{2\text{bkg}} - (P_{2\text{meas}}(f \sim 0)/P_{3\text{meas}}(f \sim 0)) * (P_{3\text{meas}} - P_{3\text{bkg}})$$

The background corrected power spectrum,  $P_{\text{corrected}}$ , would then be inverted to obtain the particle size distribution.

The correction described previously for Idiff removes common mode noise between the scattered heterodyne signal and the laser monitor. This correction is made directly to the signal. While this technique is useful in the case of dynamic light scattering and many other heterodyne systems, another method may be more easily implemented to correct the power spectrum in dynamic light scattering, for the noise component due to laser noise. In most cases the local oscillator is adjusted to provide shot noise limited detection, However, usually some excess laser noise (included in laser noise in the following description), beyond the shot noise, is observed. We will start with some definitions for power spectral densities which are all functions of frequency  $f$ :

$P_{\text{sd}}$  = total power spectral density of the scattering detector (detector 1 for Figures 5, 6, and 7 and detector 2 for Figure 19)

$P_{\text{sc}}$  = power spectral density component of the scattering detector current due to particle scattering

$P_{\text{ssh}}$  = shot noise component of power spectral density of the scattering detector

$P_{\text{sls}}$  = laser noise component of power spectral density of the scattering detector

$P_{ld}$  = total power spectral density of the laser monitor detector  
(detector 2 for Figures 5, 6, and 7 and detector 1 or 3 for  
Figure 19)

$P_{lsh}$  = shot noise component of power spectral density of the  
laser monitor detector

$P_{lls}$  = laser noise component of power spectral density of the  
laser monitor detector

$I_{os}$  = mean detector current of the scattering detector

$I_{ol}$  = mean detector current of the laser monitor detector

$P_{ssh} = 2 * e * (I_{os})$  (scatter detector shot noise)

$P_{lsh} = 2 * e * (I_{ol})$  (laser monitor detector shot noise)

Where  $e$  is the electron charge

$P_{sls} = B * g(f, ic) * ((I_{os})^2)$  (scatter detector laser noise  
component)

$P_{lls} = B * g(f, ic) * ((I_{ol})^2)$  (laser monitor detector laser noise  
component)

Since these noise sources and scattering signals are  
uncorrelated, the following equations hold:

$$P_{sd} = P_{sc} + P_{ssh} + P_{sls}$$

$$P_{ld} = P_{lsh} + P_{lls}$$

$$P_{sd} = (P_{sc} + 2 * e * (I_{os}) + B * g(f, ic) * ((I_{os})^2)) * G_s(f)$$

$$P_{ld} = (2 * e * (I_{ol}) + B * g(f, ic) * ((I_{ol})^2)) * G_l(f)$$

Where  $B$  is a constant, which describes the ratio of noise power to square of the average current, and  $g(f, i_c)$  is the spectral function for laser noise,  $f$  is frequency and  $i_c$  is laser current.  $G_s(f)$  and  $G_l(f)$  are the electronic spectral gain of the detector electronics for the scatter detector and laser monitor detector, respectively.

From these last two equations, we want to determine  $P_{sc}$ , the power spectrum component due to the light scattered from the particles. Solving these two equations for  $P_{sc}$ , we obtain:

$$P_{sc}(f) = (P_{sd}(f)/G_s(f) - (2 * e * I_{os})) - (((P_{ld}(f)/G_l(f) - (2 * e * I_{ol}))) * (I_{os}^2)/(I_{ol}^2))$$

This equation assumes that the excess laser induced amplitude noise (noise in excess of the shot noise) is proportional to the mean detector current due to the laser. This assumption is described by the proportionality to the square of the mean detector currents of power spectral density in the following equations:

$$P_{sls} = B * g(f, i) * (I_{os})^2 \quad (\text{scatter detector laser noise component})$$

$$P_{lls} = B * g(f, i) * (I_{ol})^2 \quad (\text{laser monitor detector laser noise component})$$

However, in general the excess noise components may have a more complicated and unknown dependence given by the function  $g_n$ :

$$P_{sls} = B * g_n(f, i, I_{os}) \quad (\text{scatter detector laser noise component})$$

$$P_{lls} = B * g_n(f, i, I_{ol}) \quad (\text{laser monitor detector laser noise component})$$

In this case, the functional dependence  $g_n(f, i, I)$  could be determined by measuring  $P_{sls}$  and  $P_{lls}$  at various levels of  $I_{os}$  and  $I_{ol}$ . Since the function  $g_n(f, i, I)$  could possibly change between lasers, an easier method is to adjust the mean detector currents,  $I_{os}$  and  $I_{ol}$ , to be equal with a variable optical attenuator, such as two polarizers with adjustable rotation angles. This attenuator could be placed on front of either the heterodyne detector or the laser monitor detector (as shown by detector 3 in Figure 19 for example). When  $I_{os}$  and  $I_{ol}$  are made equal, we obtain:

$$P_{sc} = (P_{sd}/G_s(f)) - ((P_{ld}/G_l(f)))$$

Another method is to measure  $P_{sd}$  and  $P_{ld}$  without any particles in the beam and calculate the ratio  $RT$  as a function of frequency:

$$RT(f) = P_{sd}(f)/P_{ld}(f) \quad \text{measured without particles in the sample volume}$$

$$\text{Then } P_{sc}(f) = P_{sd}(f) - (RT(f) * P_{ld}(f)) \quad \text{measured with particles in the sample volume}$$

This is only an estimate to the true correction, but it may work well in cases where the excess noise and mean detector currents do not vary significantly.

Notice: any products, divisions, additions, or subtractions in this document between functions (or vectors) are assumed to be inner operations (i.e. the function(x) values at each value of x are multiplied, divided, added, or subtracted).

The noise correction can also be determined from background measurements and assumptions for the form of the power spectral density for the particles and for the noise. The power spectrum of the scatter detector current from particles under Brownian motion takes the form:

$$P(f) = 4 * I_o * I_s * (K/\pi) / (f^2 + K^2) \quad \text{for particles of a single size}$$

Where

$x^2$  is the square of quantity x

$\pi$  is constant pi

$P(f)$  is the power spectral density of the detector current

f is the frequency of the detector current

$I_o$  is the detector current due to the local oscillator intensity

$I_s$  is the detector current due to the mean scattered light intensity

$K$  is a constant which is particle size dependent

The total power spectral density measured from a group of particles is given by:

$$P_t(f) = \sum_j (4 \cdot I_o \cdot I_{sj} \cdot (K_j / \pi) / (f^2 + K_j^2)) + P_b(f)$$

Where the  $\sum_j$  is over each  $j$ th particle with scattering  $I_{sj}$  and constant  $K_j$ .

$P_b(f)$  is the power spectral density of the detector current due to background such as excess laser noise and shot noise.  $P_b(f)$  is usually measured by scatter from clean dispersant without particles. Examination of these equations provides the following approximations:

$$P_t(\infty) = P_b(f \rightarrow \infty)$$

$P_b(\infty) = B$  at high frequencies, the background spectrum is white

The spectral density  $P_b = \text{constant}$  at very high frequencies

$$P_t(f \rightarrow \infty) = A / (f^2 + C) + B \quad \text{at moderately high frequencies } f \gg K_j$$

Where  $A$ ,  $B$ , and  $C$  are constants to be determined.

This dependence is illustrated in Figure 24, which shows the measurement of  $P_t(f)$  in three different frequency bands. This can be accomplished by integration of the digitally generated power spectral density over these frequency bands or by using analog electronic filters and RMS modules to measure the power in the bands. These bands must be chosen at frequencies where the approximations, which are shown above, hold. The analog filters have an advantage, over digitally generated power spectrum measurements, that they can be placed at very high frequencies without affecting the design of the analog to

digital converter and FFT algorithm used to measure the lower frequency power spectrum of the scatter signal from the particles. Then we can solve for B by using the following simultaneous equations to solve for A, B, and C:

$$P_t(f_1) = A/(f_1^2 + C) + B$$

$$P_t(f_2) = A/(f_2^2 + C) + B$$

$$P_t(f_3) = A/(f_3^2 + C) + B$$

Where  $P_t(f_1)$  is the mean power spectral density in the band about frequency  $f_1$ , and likewise for  $f_2$  and  $f_3$ .

If the frequency bands are at very high frequencies then  $f^2$  is much greater than C and the following two simultaneous equations can be used to solve for B:

$$P_t(f_1) = A/(f_1^2) + B$$

$$P_t(f_2) = A/(f_2^2) + B$$

And B is then given by:

$$B = (P(f_1)*f_1^2 - P(f_2)*f_2^2)/(f_1^2 - f_2^2)$$

Usually B is not a stable value and can change between successive digitized data sets (digitization of the detector current over a certain measurement period) and their corresponding power spectral density calculations. However, the calculation, shown above, will determine the specific value of B for each data set and calculation of  $P_t(f)$  for that data set .

$P_b(f)$  can be calculated from the value of B by using the following procedure. Measure  $P_b(f)$  and B from the background signal of clean dispersant without particles. In this case B is simply the value of  $P_b(f)$  at a very high frequency where  $P_b(f)$  has a white noise spectrum. Let  $B_0 = B$  and  $P_{b0}(f) = P_b(f)$  from this clean dispersant measurement. Then when  $P_t(f)$  and B are measured from a particle dispersion by the method described previously,  $P_b(f)$  can be determined by:

$$P_b(f) = P_{b0}(f) - B_0 + B$$

$P_b(f)$  can also be calculated from a function of B or by using a lookup table, either which can be produced by many measurements

of  $P_b(f)$  for various values of  $B$ , by simply monitoring the instrument for a few days under different starting and environmental conditions. For example  $P_b(f)$  could be fit to a polynomial, in  $f$ , whose coefficients are functions of  $B$ :

$$P_b(f) = B + G_1(B)*f + G_2(B)*f^2 + G_3(B)*f^3 + \dots$$

And then the power spectrum of the signal component due to particle scattering is given by subtracting the background power spectrum,  $P_b(f)$  (calculated from the polynomial and  $B$ ), from the measured power spectrum  $P_t(f)$ :

$$P_p(f) = P_t(f) - P_b(f)$$

This power spectral density  $P_p(f)$  can then be inverted to produce the particle size distribution or it can be integrated on a logarithmic scale for deconvolution. This process can also be used directly with the logarithmic scale power spectral data. On the logarithmic frequency scale the following variable transformations are made:

$$x = \ln(f) \quad (\ln \text{ is the natural logarithm})$$

$$f = \exp(x)$$

Then creating the power spectrum on the logarithmic scale,  $R(x)$  we obtain:

$$R(x) = P_t(f) * \partial f / \partial x = f * P_t(f) = P_l(x) = A / (\exp(x) + C \exp(-x)) + B * \exp(x)$$

We can now measure the power in three logarithmic frequency bands, analogous to  $f_1$ ,  $f_2$  and  $f_3$  in the previous description. For example the three simultaneous equations now become:

$$R(x_1) = A / (\exp(x_1) + C \exp(-x_1)) + B * \exp(x_1)$$

$$R(x_2) = A / (\exp(x_2) + C \exp(-x_1)) + B * \exp(x_2)$$

$$R(x_3) = A / (\exp(x_3) + C \exp(-x_3)) + B * \exp(x_3)$$

Where  $R(x)$  is the spectral power in the logarithmic frequency band at logarithmic frequency  $x = \ln(f)$ . And  $A$ ,  $B$ , and  $C$  are new constants to be determined from solution of the simultaneous equations and  $B * \exp(x)$  is the white noise background to be subtracted from the power spectrum measured in analogy to the linear frequency case described above.  $R_b(x)$  can be calculated

from the value of B by using the following procedure. Measure  $R_b(f)$  and  $B \cdot \exp(x)$  from the background signal of clean dispersant without particles. In this case  $B \cdot \exp(x)$  is simply  $R_b(x)$  at a very high frequency where  $P_b(f)$  has a white noise spectrum. Let  $B_o = B$  and  $R_{bo}(x) = R_b(x)$  from this clean dispersant measurement. Then when  $R_t(x)$  and B are measured from a particle dispersion by the method described previously and the simultaneous equations are solved for B,  $R_b(x)$  can be determined by:

$$R_b(x) = R_{bo}(x) - B_o \cdot \exp(x) + B \cdot \exp(x)$$

$$R_p(x) = R_t(x) - R_b(x)$$

$R_p(x)$  is the portion, of the power spectrum on the logarithmic frequency scale, which is due to particle scatter.  $R_p(x)$  is deconvolved by known methods to produce the particle size distribution.

In all of the power spectrum methods described above, all of the digitized signal samples collected from the particle dispersion consist of a group of data sets, which are collected sequentially. Each data set consists of a group of sequential digitized samples of the signal. In all of the cases described above, the power spectrum for each data set is corrected by calculations using measurements made during that set of digitized signal samples. The change of the power spectrum background should not be significant during any one data set, so that the power spectrum from each data set is corrected using the most accurate correction parameters present during the period of that data set. All of these corrected power spectra are then added together to obtain the final corrected power spectrum. This could also be accomplished by adding up all of the uncorrected power spectra and all of the corrections (corrected background to subtract from the measured power spectrum), and then subtract the sum of corrected backgrounds from the sum of measured power spectra to obtain the final corrected power spectra. The only requirement is that the corrections must be calculated at sufficiently short intervals such that the background characteristics can be accurately described by one set of parameters during any single data set,



even though the background may be changing significantly during the entire data collection period.

Another improvement to signal to noise can be gained by analog filtering of the scatter signal before signal digitization and calculation of the power spectrum. The following equation describes the power spectral density of the scatter detector current, as described before:

$$P(f) = 4 \cdot I_o \cdot I_s \cdot (K/\pi) / (f^2 + K^2)$$

This function is maximum at  $f = 0$  and drops off at higher frequencies as shown in figure 24.  $I_s$  is proportional to the square of the particle diameter for larger particles and to the sixth power of the diameter for smaller particles.  $K$  is inversely proportional to the particle diameter. So smaller particles produce more high frequency scatter signal, but with much lower amplitude. Since these low amplitude high frequency signals are mixed with high amplitude low frequency signals, the analog to digital conversion (ADC) bit error noise shows higher percentage errors for the smaller particles. One method to reduce these errors is to use an analog filter before the ADC to attenuate the lower frequency components more than the high frequency components and use either higher optical intensity or electronic gain to increase the signal to fill the range of the ADC. In this way the spectrum of the scatter signal is made more spectrally uniform before digitization to provide uniform percentage signal error due to ADC bit quantization. After the signal is digitized and the power spectrum is created, the power spectrum can be divided by the power spectral transmission vs. frequency values from the analog filter to restore the original spectrum of the signal before the filter.

Another method to reduce noise in the scatter signal is to measure self-beating (homodyning) instead of heterodyning. Figure 20 shows a homodyning scatter probe which uses pinholes to define a scatter interaction volume with the source beam. Lens 1 focuses the source beam through a mirror and an optical window with two concave surfaces which have a common center of curvature. The particle dispersion fills the concave surface which is closest to the focus spot or interaction volume. Two scatter detectors collect scattered light through pinholes which

view a volume common with the best focus volume of the source. This common volume is called the interaction volume because only particles in this volume can interact with the source beam and produce scattered light at the detectors. Detectors 1 and 2 collect scattered light through pinholes 1 and 2 respectively and lenses 3 and 2 (collector lenses) respectively. These detectors provide dynamic scattering signals from two different scattering angles, which may provide better particle size information. The entire optical assembly could be placed into a probe enclosure which could be inserted directly into the particle dispersion. Also more scattering angles could be measured by adding more collector lens/pinhole/detector assemblies which all view the same volume through the concave surfaces. The possibly expensive double concave surface optic could also be replaced by a standard plano concave lens and a prism as shown in the bottom portion of Figure 20. Also, lenses 1, 2 and 3 could be replaced by a single lens, which focuses the source light and collects the scattered light.

This system is designed to measure dynamic light scattering in the homodyne mode, without a local oscillator which usually causes scatter signal noise. Both detectors only see scattering from the interaction volume which could be very close to the inner concave surface, providing very short optical path for scattered rays and reduced multiple scattering at high particle concentrations. This configuration may have advantages when measuring very small particles whose scattering signal is lost in the fluctuations of the background signal caused by small fluctuations in the large local oscillator needed for heterodyne detection. However, in some cases (larger particles for example), heterodyne detection is still the optimal detection means. Figure 23 shows how the ideas in Figure 20 can be adapted for heterodyne detection by using fiber optics and fiber optic couplers to distribute and mix source light with the scattered light at each detector. Lens 4 focuses the source light into the fiber optic which guides the light to lens 1 as shown in figure 20. A portion of the light is split off by a fiber coupler 1 and distributed, by coupler 3, to other couplers, 2 and 4, which mix the source light with the scattered light which is collected by lenses 2 and 3, respectively. Scattered light which is collected by lens 2 or lens 3 is guided by each of two separate

fiber optics to scatter detectors 2 or 1, respectively. The source light from fiber coupler 1 is split by fiber coupler 3 to be distributed to fiber couplers 2 and 4 for mixing with scattered light for detectors 2 and 1, respectively. This fiber optic system could also be replaced by the analogous waveguide structures in an integrated optic chip.

Another configuration for using the design, shown in Figure 20, in heterodyne mode is shown in Figure 22. This concept is very similar to that in Figure 20, except that a portion of the source beam is split off by beam splitter 1 to be combined with the scattered light on scatter detector 2 through beam splitter 2. This configuration provides two advantages: the high signal to noise of heterodyne detection and very low back reflection into the light source. Back reflection into laser sources can cause excess laser noise. The back reflections can be further reduced by anti-reflection coating of optical surfaces, in particular, the first air-glass surface of the concave optic. Figure 22 shows the combination of a heterodyne channel (detector 2) and a homodyne channel (detector 1). However, the source light transmitted through beam splitter 2 could also be combined with the detector 1 scattered light using a third beam splitter to produce a second heterodyne channel. Figure 21 shows a method for creating the concave optic from two or three mass produced optics. A plano-convex lens and plano-concave lens are positioned so that the centers of curvature for their curved surfaces are coincident at the interaction volume. If required, a plano spacer can be placed between these two optics. In any case, all plano surfaces can be bonded to the adjacent plano surface with index matching adhesive to reduce internal reflections.

One source of signal noise in fiber optic dynamic light scattering systems is interferometric noise due to motion of the optical fibers. This noise can occur in both single and multimode fiber optics and couplers. Figures 25 and 26 show two concepts for reducing the fiber motion by potting the fiber optic assembly in a solid potting material, which can be cured from a liquid to a solid. Most potting materials will work well, but materials with high thermal conductivity and/or low thermal coefficient of expansion may be most appropriate. Figure 25

shows the fiber optic system, from Figure 19, potted with fiber optic connectors to the light source and detectors which remain outside of the potted volume (but one half of each connector is potted into the potted volume). This provides for replacement of the detector or light source. Figure 26 shows the same fiber optic system which is entirely potted, with access to the detectors and light source through electrical connections needed for powering and monitoring the source and detector. See Figure 19 for port designations. The detector at port three can also be outside of the potted volume and connected by a fiber optic connector to port 3 (as shown in Figure 25 for port 2) or it could be potted into the structure and accessed through an electrical conduit as shown in Figure 26 for port 2. In Figure 26, the optical path must be kept free of potting material to avoid attenuation or distortion of the optical beam. These voids in the potting volume are not explicitly shown in Figure 26. Depending upon the mechanism creating the interferometric noise, the fiber optic cable sheath and/or fiber optic buffer could be removed so that the potting material adheres directly to either the buffer or the cladding of the fiber. Or In cases where only the cable needs to be immobilized and the fiber can be allowed to move within the cable, the cable can be left on the fiber. Then the potting material will adhere to the cable surface. In any case, this potting method should reduce the frequency and amplitude of the fiber motion induced noise so that it can be removed from scatter signal as a small correction.

Figure 27 shows another version of the fiber optic system, where the source light is mixed with the scattered light through fiber optic port 3. In this case, the surfaces in the scatter collection optics, at port 4, and in the optics at port 3 are anti-reflection coated to avoid back reflections of source light into port 2. This provides two advantages. Firstly, the amount of light out of port 3 can be much larger than the light that was intentionally back reflected from port 4, in Figure 10, creating a larger local oscillator. Additionally, very little light is back reflected into the light source in this design. Back reflection into laser sources can cause excess laser noise. In all of the cases shown in this disclosure, back reflection into light source can be reduced by use of a polarizer and quarter wave plate to produce an optical isolator at the exit of

the light source assembly. However, this requires the use of expensive single mode polarization preserving fiber optics and couplers; and it produces circular polarized light at the particles. And it will also not work with multimode fiber optics. However, this disclosure claims the use of an isolator to reduce back reflections into the laser to reduce laser amplitude and phase noise in this application, when it is appropriate.

In some cases, very large particles can contribute scatter signals which will distort the signals from smaller particles. In this case, particle settling could be used to remove larger particles from the interaction volume, as shown in Figure 28 which shows a variation on the concept in Figure 9. The sample chamber has an extension above the interaction volume so that particles cannot settle into the interaction volume from above. Hence, the interaction volume will gradually be depleted of larger particles, which settle out of the volume. Scatter data can be collected at various times during this settling process to measure different size ranges of the distribution separately. The bottom portion of the sample cell enclosure is shortened or removed completely to allow the particle dispersion to flow down and out of the interaction volume when the sample cell is emptied and rinsed in preparation for the next sample.

As mentioned before, one cause of laser noise is laser light which is reflected back into the laser. Figures 29 and 30 show versions of Figures 4 and 8, respectively, where a polarizing beamsplitter and quarter wave plate are utilized to increase the optical efficiency of the detection path and reduce the light back-reflected into the laser. The polarizing beam splitter is oriented to provide maximum transmission for the polarization of the laser. The polarized light passes through a quarter wave plate with axes at 45 degrees to the polarization direction of the source. The local oscillator light, which is reflected back from the convex surface in Figure 29 or from the partial reflecting mirror in Figure 30, will pass back through the quarter wave plate on the return path towards the polarizing beamsplitter. In both cases, the light gains a second quarter wave of phase in one polarization, accumulating a total of one

half wave which will rotate the polarization by 90 degrees. When passing back through the polarizing beamsplitter, the 90 degree polarization rotated light will be reflected by the beamsplitter and very little light will transmit through the beamsplitter to be focused back into the laser source. The scattered light will propagate through the same process, and also be reflected by the polarizing beamsplitter. So both the source light and scattered light will be reflected by the polarizing beamsplitter through the lens 4 to the detector, where mixing, of the local oscillator and scattered light, and heterodyne detection of the scattered light occurs. Any flat surfaces between lenses 2 and 3, except for a surface which reflects the local oscillator, shall be tilted slightly, and/or anti-reflection coated, so that the reflection from that surface will not pass into the laser source. For example, the beamsplitter and quarter wave plate should both be tilted slightly off of normal to the optical axis so that reflections from their surfaces cannot pass back to the laser. All of these surfaces, except for those reflecting the local oscillator reflection, should also be anti-reflection coated. One end of a fiber optic (preferably polarization preserving fiber optic) with an attached scattering optic assembly on the other end, as shown previously in this disclosure, could also be aligned with the final light source focal point (in the interaction volume) of either Figure 29 or Figure 30 to provide a flexible extension and scattering probe. In this case, the local oscillator could be created by a reflecting surface inside of the scattering optics assembly, which contacts the particle dispersion, so that the scattered light and local oscillator travel through the same optical paths to get to the detector. The other end of the fiber optic could also be immersed directly into the particle dispersion without any scatter optics. This extension could also be used with the systems in Figures 1 through 8, with multimode or single mode fiber optics.

### **Other Noise Correction Techniques**

The basic fiber optic interferometer is illustrated in Figure 10. A light source is focused into port 1 of a fiber optic coupler. This source light is transferred to port 4 and light

scattering optics which focus the light into the particle dispersion and collect light scattered from the particles. This scattered light is transferred back through the fiber optic and coupler to the detector on port 2. If the coupler has a third port, a portion of the source light also continues on to port 3 which may provide a local oscillator with a reflective layer. If the local oscillator is not provided at port 3, a beam dump or anti-reflective layer may be placed onto port 3 to eliminate the reflection which may produce interferometric noise in the fiber optic interferometer. The beam dump could consist of a thick window which is attached to the tip of the fiber with transparent adhesive whose refractive index nearly matches that of the fiber and the window. This will reduce the amount of light which is Fresnel reflected back into the fiber at the fiber tip. The other surface of the window can be anti-reflection coated, and/or be sufficiently far (thick window) from the fiber tip, to minimize the reflected light, from that surface, that can enter the fiber.

Figure 11A shows one version of the scatter optics on port 4. A lens or gradient index optic (GRIN) focuses the source light into the particle dispersion in a cuvette through a transparent wall of the cuvette. A partially-reflective layer on the tip of the fiber or on the surface of the GRIN rod, at the fiber/GRIN gap, provides the local oscillator light to travel back through port 4 with light scattered by the particles. If the fiber surface is partially reflecting, the GRIN surface could be anti-reflection coated or it could be placed sufficiently far from the fiber to avoid reflections from the GRIN surface back into the fiber. Reflections from both surfaces could produce an optical interference signal which may contaminate the heterodyning signal from the scattering particles. The reflected source light and the scattered light, from particles in the cuvette, travel back through the coupler and are combined on the detector at port 2. The interference between these two light components is indicative of the Brownian motion of the particles and the particle size. Since the local oscillator is generated at the exit surface of port 3 or port 4, as opposed to the cuvette surface, the interference signal is not degraded by small errors in the position of the cuvette surfaces, allowing use of inexpensive disposable cuvettes. The local oscillator is

provided by light reflected from either port 3 or port 4 fiber optic.

Other designs for port 4 could incorporate a window, on the surface of the GRIN rod, which contacts the particle dispersion directly.

The port 2 detector current is digitized for analysis to determine the particle size in the dispersion. The power spectrum of the optical detector current contains a constant local oscillator and a frequency dependent component. The frequency dependent component is described by the following equations:

$$P(f) = (S(d,a,nm,np)^2) * (D * K^2) / (4\pi^2 * (f)^2 + (DK^2)^2) + n(f)$$

where  $K = 2 * nm * \sin(a/2) / \lambda_l$

$$D = kT / (3 * \pi * \eta * d)$$

$P(f)$  = power spectral density of the detector current (or voltage) at frequency  $f$

$S$  = scattering efficiency per unit particle volume

$d$  = particle diameter

$\eta$  = dispersant viscosity

$f$  = frequency

$np$  = refractive index of particle

$nm$  = refractive index of dispersant

$a$  = scattering angle

$c$  = constant which depends on dispersant viscosity and particle shape

$^2$  = square of quantity

$g$  = acceleration

$k$  = Boltzman's constant

$T$  = dispersant temperature

$\lambda_l$  = wavelength of the source light

$n(f)$  = baseline noise power spectral density

This equation describes the power spectrum from a single particle of diameter  $d$ . For groups of particles of various sizes, the power spectrum is the sum of the spectra from the individual particles. Then the total spectrum must be



deconvolved to find the particle size distribution. Usually the spectrum from clean dispersant is measured to determine  $n(f)$ , which is the portion of the spectrum due to laser noise, detector noise, modal interference due to fiber optic vibrations, and other noise sources. This baseline noise is the power spectrum measured without any particles in the dispersant. This baseline noise spectrum is subtracted from the power spectrum measured from the particles to determine the spectrum which is only due to Brownian motion of the particles. However,  $n(f)$  is not usually stable during the period required to gather sufficient digitized data to create an accurate estimation of the power spectrum.

One useful property of the fluctuating portion of the baseline noise is that the noise is nearly white and shows strong correlation with values of  $n(f)$  at high frequencies. As shown by the equation for  $P(f)$ , the power spectrum component due to light scattered from the particles drops off very rapidly at high frequencies and becomes negligible as compared to  $n(f)$  at high frequencies. At high frequencies, the particle scatter portion of the spectrum drops as  $1/f^2$ . In any event the detector current could be sampled at sufficiently high frequencies to measure the power spectrum where the contribution from the particles is small.

One method for noise correction is to generate an empirical set of  $n(f)$ 's by measuring  $n(f_p)$  in the frequency region where the particles contribute to  $P(f)$  while also measuring  $n(f_h)$  at high frequencies where the particle contribution would normally be small. So various  $P(f)$  samples are measured without particles to generate a function  $G$ :

$$n(f_p) = G(n(f_h))$$

The portion of the spectrum  $n(f_h)$  could be measured from the calculated power spectrum of the digitized data. But then the detector current must be sampled at rates well beyond those required to measure the particles. The value for  $n(f_h)$  could also be measured by band pass analog filters and power circuits, to generate the total power in a bandpass in frequency

regions which capture frequencies where the particles will have very small contributions.

In either case, once the function  $G(n(f_h))$  is created, it can be used to correct the spectrum measured from particles by measuring  $n(f_h)$  each time a data segment is recorded by digitizing the scatter detector current for a short period and an FFT is created to produce the contribution of this short period signal to the total power spectrum of the entire measurement period. This particular  $n_i(f_p) = G(n_i(f_h))$  is then subtracted from the  $P_i(f)$  for the  $i$ th data segment to correct that data segment for the  $n(f)$  during that segment. In this way, as  $n_i(f)$  fluctuates, the  $i$ th data segment is corrected precisely for the noise in that segment. This could also be accomplished by summing all of the  $P_i(f)$ 's over  $i$  to get  $P_t(f)$  and all of the  $n_i(f)$ 's over  $i$  to get  $n_t(f)$  and then using  $P_t(f) - n_t(f)$  to calculate the spectrum contribution from the particles.

$G(n(f_h))$  could also be determined from data points in both the upper  $f_p$ , and  $f_h$  regions to produce better conditioning of the simultaneous equations used to solve for the parameters in the function  $G$ . In any case, if the fluctuating component of  $n(t)$  is white noise and is flat out to  $f_h$ , then the correction is simple because  $n(f_p) = n(f_h)$ . But in general, a function  $G$  may be required to get precise correction over the entire range of fluctuations.  $G$  can take the form of a polynomial function of  $f$  (over both regions  $f_p$  and  $f_h$ ) or a group of  $n(f_p)$  functions in a look-up table, where interpolation between the 2 table  $n(f_p)$  functions, with the closest corresponding values for  $n(f_h)$  to the measured value of  $n_i(f_h)$ , would be used to determine the  $n_i(f_p)$  for the  $i$ th data segment. In some cases,  $G$  will be proportional to the inverse of the square-root of frequency  $f$ .

This correction procedure is only required in the frequency regions where the fluctuations in  $n(f)$  cause unacceptable errors in the calculated particle size distribution. Typically this will be in the higher frequency end of the  $f_p$  region, where the smaller particle information is contained. At lower frequencies, a single measurement of  $n(f)$  before or after the particle measurement may be sufficient, without using  $G$ .

Another method which may be utilized is to solve entire the problem in a generalized fashion. This method would use all of the power spectrum data,  $P(f_p)$  and  $P(f_h)$ , to solve for the particle contribution and baseline contribution using an iterative procedure (optimization or search algorithm) which assumes the existence of both. However, the G function method described above may be more effective because more apriori knowledge is provided to the algorithm.

These methods can be applied to the power spectrum on any frequency scale, including but not limited to a logarithmic progression in  $f$ . However, if the fluctuating portion of the baseline noise is nearly white or uniform in density, then a linear scale in  $f$  may be optimal for calculation of G.

The background can be solved for as part of the total solution in this background drift problem and many other similar problems where a system model is inverted to solve for the particle size distribution. Consider the generalized model below:

$$F = H*V$$

Where  $F$  is the measured data (power spectrum of scattered light signal, angular distribution of scattered light, etc.),  $V$  is the size distribution to be solved for, and  $H$  is the matrix which describes the system model (Brownian motion/Doppler effect, angular light scattering, etc.). This model is usually inverted to produce the size distribution:

$$V = F/H \quad (\text{a matrix inversion, not a literal division})$$

Where  $F/H$  represents the solution of the matrix equation by any means including iterative techniques with constraints on the values of  $V$ . The actual values for  $F$  are calculated by subtraction of the actual background from the measured  $FB$ , which includes the background.

$$FB_{\text{measured}} = F_{\text{actual}} + B_{\text{actual}}$$

Where  $F$  and  $B$  are the actual scattering data and the background (without particles), respectively.

However the computed values (called  $F_c$ ) for  $F$  use the measured values of  $B$  which may differ from the actual values of  $B$  (due to drift of  $B$ ) by the error vector  $E$ .

$$B_{\text{actual}} = B_{\text{measured}} + E$$

$$F_c = FB_{\text{measured}} - B_{\text{measured}}$$

$$F_c = F_{\text{actual}} + E$$

Then the matrix equation above becomes:

$$F_c - E = H*V$$

Solving this matrix equation for  $V$ , we obtain

$$V = (F_c - E)/H \quad (// \text{ is not a literal division, } / \text{ represents solution of the matrix equation above for } V)$$

If  $V$  has  $m$  unknowns,  $F$  has  $n$  measured values, and  $E$  is described by  $k$  number of parameters, then  $V$  and  $E$  can be solved from this equation as long as  $m + k \leq n$ . This method works well when  $E$  is much smaller than  $B_{\text{measured}}$  so that the correction  $E$  is small and accurately described using only a few parameters. For example, in the previous case,  $E$  could be simply white noise times a constant which determines the amount of white noise which must be added to the noise background, which was measured without particles in the source beam.  $E$  is determined to obtain the best result for  $V$ , or in other words the result which minimizes the RMS error:

$$\text{SQRT}(\text{SUM}((F_c - E) - (H*V))^2)$$

Where  $\text{SUM}$  is the summation over the vector elements. This function can be minimized by known iterative methods, such as simply changing  $E$  and inverting  $F_c - E = H*V$  multiple times and choosing the result for  $V$  and  $E$  which minimizes the RMS error above.

Figure 10 shows a fiber optic system for measuring the Brownian motion and size of particles. Figure 32 shows an extension of this idea, where port 4 is designed as a probe tip with integral

window. The probe is immersed into the particle dispersion and the Fresnel reflection, from the interface between the window and the dispersion, provides the local oscillator light for heterodyne detection by providing a path for this reflected light to travel back through the fiber optic with the scattered light to provide the heterodyne interference signal on the detector. Single mode fiber optics have core diameters in the 5 to 8 micron range. Since this small core size will collect light from a very small volume of dispersion, larger particles may not be easily detected due to their low count per unit volume. The probability of larger particles entering this small interaction volume is small and so the signals from larger particles are sporadic and discontinuous. Figure 32 shows a high magnification configuration for the probe tip, where the core of the single mode fiber is imaged to the window/dispersion interface at high magnification. This produces a large interaction volume and better detection of larger particles. All of the optical surfaces in the probe can be antireflection coated, except for the surface which interfaces with the dispersion and produces the local oscillator reflection. Also the GRIN rod could be designed to fill the entire space between the fiber optic tip and the window; or the window thickness could be increased to produce only a small gap separation between optical components. Then all gaps between optical components could be filled with refractive index matching gel or epoxy to reduce reflections. Also the GRIN rod could be replaced by antireflection-coated conventional spherical or aspherical optics which provide the required magnification. This design could also be used with homodyne systems by projecting the image of the core tip into the dispersion, reducing the amount of light, which is Fresnel reflected back into the fiber core, or by antireflection coating of the dispersion/window interface. This dispersion/window surface coating must account for the refractive index of the dispersion to minimize the reflection at the dispersion/window interface. For example, a magnification of 5 will provide a 40 micron diameter illumination region (and scattered light collection region) at the dispersion/window interface from an 8 micron core single mode fiber optic. This larger region will provide both larger width and larger depth for the effective scattering volume in the dispersion, because particles can contribute scattered light farther from the window/dispersion

interface due to the larger diameter illumination and larger diameter scattered light collection region. The scattering volume should be large enough to provide significant probability (>50%) for containing one of the particles, of interest, at the lowest number concentration. The size of this scattering volume and the corresponding optical magnification will depend upon the number concentration of the particles with the lowest number concentration in the particle size distribution. These are usually the largest particles. Magnifications beyond 5 may be required for lower number concentrations or magnifications less than 5 for higher number concentrations.

### **Small Particle Detector for Large Fluid Volumes**

Semiconductor processes require very clean fluids with less than one 0.1 micron particle per cubic meter. The light scattered by a particle of this size can be detected as it passes through a focused laser beam. However at 10 meters per second flow rate, interrogation of a cubic meter of fluid would consume over 3 years through a laser volume of 1000 cubic microns (cubic volume of 10 microns on each side). This invention describes an apparatus for detecting the presence of one particle per cubic meter at a rate of 1 cubic meter per hour. The system is shown in Figure B1.

A light source is projected into a sample flow tube by lens 1, as shown in Figure B1. The optics may be adjusted to collimate the beam within the tube or to produce a beam waist inside the tube. Beam splitter 1 reflects a portion of the beam onto lens 2 which focuses that light onto detector 2. Detector 2 measures the source intensity to correct for source fluctuations. The unreflected portion of the beam proceeds through beamsplitter 2 which reflects a portion of the beam back through lens 3, providing a local oscillator for heterodyne detection of scattered light from particles in the sample flow tube. The unreflected portion of the beam proceeds through optical window 1 and travels down a long sample tube, through which the test fluid is pumped. Window 2 allows the beam to exit the tube with minimal reflections back into the tube. Any particle passing down the tube will scatter light back to detector 1 through beam splitter 1, lens 3 and a pinhole which maintains coherence

requirements for heterodyne detection and eliminates background light from hitting detector 1.

The major advantage of this system is the large cross-section of the interrogated volume in the sample flow tube and the long interaction distance within the tube, which could be meters in length. The two normalized (detector responsivity = 1) detector currents,  $I_1$  from detector 1 and  $I_2$  from detector 2, can be described by the following equations:

$$I_1 = \sqrt{R_1 T_1 R} \sqrt{I_o(t) * I_s(t)} * \cos(F * t + A) + R_1 T_1 R I_o$$

$$I_2 = K R_1 I_o(t)$$

where:

$\cos(x)$  = cosine of  $x$

$K$  is a constant which describes the ratio of other efficiencies (optical and electrical), between the  $I_1$  and  $I_2$  channels, which are not due to the beamsplitters.  $R$  and  $T$  are the reflectivity and transmission of beamsplitter 2, respectively.  $R_1$  and  $T_1$  are the reflectivity and transmission of beamsplitter 1, respectively.

$\sqrt{x}$  = square root of  $x$

$I_o(t)$  is the source beam intensity as function of time  $t$

$F$  is the heterodyne beat angular frequency at detector 1 due to the motion of the scatterer in the flow tube. And  $A$  is an arbitrary phase angle for the particular particle.  $I_s(t)$  is the scattered light intensity from the particle:

$I_s(t) = S T_1 R_1 T T I_o(t)$  where  $S$  is the scattering efficiency for the particle.  $S$  includes the product of the scattered intensity per incident intensity and optical scatter collection efficiency.

The light source intensity will consist of a constant portion  $I_{oc}$  and noise  $n(t)$ :

$$I_o(t) = I_{oc} + n(t)$$

We may then rewrite equations for  $I_1$  and  $I_2$ :

$$I_1 = R_1 T_1 T \sqrt{S R} (I_{oc} + n(t)) \cos(F t + A) + R_1 T_1 R (I_{oc} + n(t))$$

$$I_2 = K R_1 (I_{oc} + n(t))$$

The heterodyne beat from a particle traveling with nearly constant velocity down the flow tube will cover a very narrow spectral range with high frequency  $F$ . For example, at 1 meter per second flow rate, the beat frequency ( $F/(2\pi)$ ) would be in the megahertz range. If we use narrow band filters to only accept the narrow range of beat frequencies we obtain the narrow band components for  $I_1$  and  $I_2$ :

$$I_{1nb} = R_1 T_1 T \sqrt{S R} I_{oc} \cos(F t + A) + R_1 T_1 R n(t)$$

$$I_{2nb} = K R_1 n(t)$$

where we have assumed that  $n(t)$  is much smaller than  $I_{oc}$ .

The laser noise can be removed through the following relationship:

$$I_{diff} = I_{1nb} - (T_1 R / K) I_{2nb} = R_1 T_1 T \sqrt{S R} I_{oc} \cos(F t + A)$$

This relationship is realized by narrowband filtering of each of the  $I_1$  and  $I_2$  detector currents. One or both of these filtered signals are amplified by programmable amplifiers, with adjustable gains. The difference of the two outputs of these amplifiers is generated by a difference circuit or differential amplifier. With no particles in the beam, the gain of at least one of the programmable amplifiers is adjusted, under computer or manual control, to minimize the output of the difference circuit. At this gain (for example gain  $I_2 = K / (T_1 R)$ ), the source intensity noise component, in the detector 1 beat signal,



is removed from the difference signal  $I_{diff}$  which is fed to an analog to digital converter (A/D), through a third narrowband filter, for analysis to sense the beat signal buried in noise. This filtered difference signal could also be detected by a phase locked loop, which would lock in on the beat frequency of current from detector 1.

Beamsplitter 2 reflection is adjusted to obtain shot noise limited heterodyne detection, with excess laser noise removed by the difference circuit. This entire correction could be accomplished in the computer by using a separate A/D for each filtered signal and doing the difference by digital computation inside the computer. If both signals were digitized separately, other correlation techniques could be used to reduce the effects of source intensity noise. The advantage of this measurement is that the high frequency beat signal is produced for the duration of the particle's residence in the long flow tube. This tube could be meters in length. This could produce millions of beat cycles during the particle's transit, allowing phase sensitive detection in a very narrow bandwidth at megahertz frequencies, well above any  $1/f$  noise sources. The power spectrum of a data set consisting of a large number of signal cycles will have a very narrow spectral width, which can be discriminated against broad band noise, by using the computed power spectrum of the signal and spectral discrimination algorithms. For example, a 1 meter long tube, with flow at 1 meter per second, will produce a heterodyne signal with a Fourier spectrum which consists of a narrow peak, with center in the megahertz range and a spectral width of a few Hertz. This signal can easily be retrieved from broadband noise by narrowband filtering or spectral analysis of the signal. If the flow variation (and Doppler frequency variation) is significant, a broader band analog filter could be used with spectral discrimination analysis of the digitized signal. For example, if the flow rate were 1 meter per second with a 1 meter flow tube, the heterodyne signal could be broken up and digitized in approximately 1 second data segments. Based upon the known variation in flow rate over long periods, the heterodyne signal would be filtered with a bandpass which covers the entire range of Doppler frequencies which span the entire flow rate variation. The Fourier transform or power spectrum of each 1 second data segment is then analyzed to find a narrow

spectral peak somewhere in the broader bandpass of this filter. While the center frequency of this peak may drift with flow rate over long periods, over any 1 second period the flow will be sufficiently constant to produce a narrow Doppler spectrum which can easily be discriminated against the broad band noise, because the spectral density of the narrow peak will be higher than that of the noise. This narrow spectrum can be insured by controlling the flow rate to be nearly constant during each particle transit time through the flow tube. The pumping system could consist of a pressurized tank (with regulator), with a flow restriction (orifice) on the outlet. The flow through this orifice may vary slowly over long periods, but over 1 second periods, the flow will be very constant, without the short term variations introduced by pumps with mechanical frequencies greater than 1 hertz.

Another system for noise reduction is shown in Figure B2, which shows only the detection portion of the system up to window 1 of the flow tube shown in Figure B1. In this case two interferometers, using detector 1 and detector 2, separately detect the oscillation of the interference signal at two different phases. The purpose is to eliminate the noise component of these signals by analysis of these phase shifted signals. For example, if the relative positions of mirror 1 and mirror 2 are adjusted to provide 180 degree optical phase shift between the two interferometers, then the two beat signals will be 180 degrees out of phase, however the common mode noise will still be in phase. Hence the difference of these signals will eliminate the common mode noise but enhance the beat signals. The source light is nearly collimated by lens 1 and focused through aperture 3 by lens 5 and then nearly collimated (or focused) by lens 6 for projection down the flow tube which contains the flowing dispersion. Scattered light from any particles in the beam passes back through lens 6, aperture 3, and lens 5 before being split off by two successive beamsplitters (beamsplitter 2 and beamsplitter 3) which use lens 3 and lens 4, respectively, to project the scattered light to detector 1 or detector 2, through pinholes. These pinholes define the range of scattering angles which are accepted by each detector. A portion of the source light is also split off by

beamsplitter 2 and beamsplitter 3 and reflected by mirror 1 and mirror 2, respectively, to provide local oscillator for heterodyne interferometry by mixing with the scattered light on detector 1 and detector 2, respectively. Mirror 1 and mirror 2 are slightly tilted (exaggerated for illustration) so that the light reflected by each mirror does enter the source through the beamsplitters and lens 1. Laser diode noise is sensitive to feedback in to the laser cavity. By tilting these mirrors, the pinhole 1 and pinhole 2 should be positioned to capture identical portions of the scattered wavefront which is parallel to the wavefront of each mirror reflection to provide nearly a single interference fringe on each detector. Then usually the mean of the scattering angle range will be slightly less than 180 degrees. In this case aperture 3 must be widened to allow passage of the source light and the scattered light, which do not pass through the same region at the plane of aperture 3. However, if laser feedback noise is not a problem, then mirror 1 and mirror 2 can operate at 90 degree reflection (relative to the source beam) and aperture 3 can be smaller to pass only the source light and scattered light over a small angular region around 180 degree scattering angle. In this case pinhole 1 and pinhole 2 could be eliminated if they do not offer any other baffling advantages, because they will provide optical blocking over the same scattering angular range as aperture 3. In general the sizes of these pinholes or apertures are chosen to only allow one fringe (or a minimum number of fringes) to be seen by each detector to maximize the beat signal amplitude on each detector. Also each detector must see the same fringe, or fringe set, so that the interferometric beat signals will be identical, but 180 degrees out of phase, on detector 1 and detector 2. The signals will have the same form as shown before:

$$S1 = \sqrt{S \cdot T1} \cdot (I_{oc} + n(t)) \cdot \cos(F \cdot t + A1) + T1 \cdot (I_{oc} + n(t))$$

$$S2 = \sqrt{S \cdot T2} \cdot (I_{oc} + n(t)) \cdot \cos(F \cdot t + A2) + T2 \cdot (I_{oc} + n(t))$$

Where T1 and T2 account for optical reflection and transmission differences between the two detector systems. After electronic filtering (either bandpass filtering at the beat frequency or high pass filtering, with cutoff below the beat frequency) we obtain the filtered version for each signal:

$$S1f = \sqrt{S*T1}*Ioc*\cos(F*t + A1) + T1*n(t)$$

$$S2f = \sqrt{S*T2}*Ioc*\cos(F*t + A2) + T2*n(t)$$

Then we use an adjustable gain, G, (and adjustable phase if needed) on one signal to balance these two detection channels. Here we have assumed that Ioc is much larger than n(t). The difference circuit, diff in Figure B2, then produces the following difference signal at the input to the analog to digital converter (A/D):

$$\text{deltaS} = S2f - G*S1f$$

The gain G can be adjusted for minimum deltaS when no particles are in the flow tube (note: this same electronic design could be used to process the signals from detector 1 and detector 2 in Figure B1). Then either mirror 1 or mirror 2 can be moved by micro-actuator to maximize the portion of deltaS at the beat frequency while a low concentration sample of particles is flowing through the flow tube. The beat frequency component of deltaS is maximized when the mirror positions provide the following optical phase difference between the detection arms:

$$A1 - A2 = m\pi \quad \text{where } m \text{ is an odd integer}$$

When these two conditions are satisfied, the following equations will be satisfied:

$$G = T2/T1$$

$$A1 - A2 = m\pi$$

$$\text{deltaS} = \sqrt{S*T2}*Ioc*\cos(F*t + A1) + T2*n(t) - (\sqrt{S*T2}*Ioc*\cos(F*t + A1 - m\pi) + T2*n(t))$$

and since  $\cos(x - m\pi) = -\cos(x)$  for m odd

$$\text{deltaS} = 2 * \sqrt{S*T2}*Ioc*\cos(F*t + A1)$$

$\delta S$  will be the pure beat signal from the moving particle without excess laser noise effects. However, residual noise sources which are not common to both channels may not be totally eliminated, such as shot noise of the individual detectors. But  $I_{oc}$  can be adjusted to sufficiently high level to provide shot noise limited heterodyne detection for both detectors, with common mode noise eliminated by the differential measurement. The residual noise can be reduced by using power spectrum calculation, correlation, or matched filters for the sinusoid at the beat frequency, which can be calculated from the flow velocity.

Laser phase noise is another possible error source. However, for systems with flow tube lengths less than 1 meter (total maximum optical path differences below 2 meters), the phase noise, even from the worst sources (laser diodes), will be below 1 milliradian RMS. This noise will be much lower for gas lasers such as HeNe lasers. If laser phase noise (or short laser coherence length) is a problem, the optical paths for mirror 1 and mirror 2 can be extended to match the average optical path for the scattering particle during travel of the particle down the flow tube. For example, if a particle at the middle of the transit down the tube is approximately 0.5 meter from the midpoint between the beamsplitters, then the mirrors should be placed 0.5 meter away also. This could also be accomplished by using coiled single mode fiber optics, with coupling lens and reflecting end, to extend the optical path of the mirror arms in a compact space. Otherwise, the open air mirror arm paths could run parallel to the flow tube to minimize the total volume of the detection system. Also lasers must be chosen with coherence lengths longer than the optical pathlength difference of each interferometer arm. This pathlength difference is slightly longer than twice the length of the active flow tube section, if the mirror arms are not extended. Certain laser diodes and most gas lasers have coherence lengths greater than 2 meters so that each particle will produce more than a million beat frequency cycles during one passage through a 1 meter long flow tube. But shorter or longer tubes will also work well, as long as the source meets the coherence length requirements.

The signal to noise is maximized by using a narrow band filter, centered at the Doppler frequency of the moving particle. However, the flow in the tube may not be constant with time and so the Doppler frequency may drift. Also laser phase noise may produce some variation of the frequency. The bandwidth of the analog narrow band filter must be sufficient to pass these frequency variations over the time scale of a complete analysis which may take hours. Therefore, the narrow band analog filter should cover the overall spectral width of long term drift. The signal which passes through this filter will be digitized directly (with difference computed after digitization), or if the signal differences are done by analog electronics, then the difference signal will be digitized as shown in figure B2. The velocity and Doppler frequency drift over one transit time of the flow tube can be much smaller than over the entire measuring time. Therefore, the data should be processed to maximize the signal to noise given the very narrow bandwidth of the signal from one transit time. The power spectrum of each digitized data set, from each successive period of one particle transit time, will produce a narrow peak at the position of the Doppler frequency for that transit time period. For example, if the average flow velocity in the tube were 1 meter per second, and the light wavelength were such that the corresponding Doppler frequency were 1 Mhz, then a flow velocity variation of 2% about this average would produce a frequency variation of 20Khz. So in this case the narrow band filter should be at least 20Khz wide. However if, during any single transit, the velocity is constant to within 10 ppm, then the power spectrum of each transit would produce a 10 Hz wide peak at the Doppler frequency of that velocity. In this way, the best signal to noise is obtained due to the excellent frequency discrimination of the power spectrum; and the narrow band filter removes unwanted signal components which would tax the common mode rejection of the difference computation or analog difference circuit. To maximize the signal to noise, the power spectrum should be computed for each transit time data set and the peak of that spectrum should be found. If that peak is sufficiently narrow and greater than a certain threshold above the background spectrum, then a particle will be counted for that data set.

In some cases, the particle size of the detected particle may be important. A second optical system, which measures lower angle scattering, can be placed into the flow tube. This system can project a beam across the flow tube to detect and count larger particles which do not require the high sensitivity of the backscatter system shown in figures B1 and B2. A laser beam is projected through two opposing windows in the sides of the flow tube. A lens collects scattered light at a low scattering angle. The beam can be shaped by anamorphic optics to produce a thin plane of light which passes through the flow stream. An additional lens can be added to collect scattered light at the angles of interest, as shown elsewhere by this inventor, but in this case the interaction volume will encompass nearly the entire cross section of the flow tube.

This 180 degree optical phase technique can also be applied to conventional dynamic light scattering systems which measure heterodyned scattered light from multiple particles, moving due to Brownian motion. The interference of the local oscillator and the scattered light from each particle will produce a signal which consists of a group of sinusoids of random phase and frequency. Each of these sinusoids will be measured by both detectors with a 180 degree phase shift between them, so that when the two phase shifted signals are subtracted, the common mode excess laser noise cancels out leaving only the signal due to Brownian motion of the particles. This double detector system can be designed as shown in figure B2, where the flow tube is replaced by a sample cell which holds a static, non-flowing, sample. This double detector can also be used in a fiber optic system using fiber optic couplers, where the local oscillator is derived from a reflector on one of the output ports of each coupler, as shown in Figure B3. Detector 1 and detector 2 have the same function as they do in Figure B2 and they would be connected to the same electronics and computer analysis as described before. As before, the optical path difference between the mirror reflected light and the scattered light must meet the following criteria for both detectors:

$$A_1 - A_2 = m\pi \quad \text{where } m \text{ is an odd integer}$$

If the optical path length of the fiber optic mirrored arms vary due to temperature or stress changes in the fiber optic, the phase of one arm could be controlled by an fiber optic phase modulator, and a feed back loop, to maintain the maximum heterodyne beat signal at the output of the difference circuit.

Figure B4 shows a system, which is similar to that shown in Figure B3, with the advantages of low light reflection feedback into the laser source, low interferometric crosstalk between detectors, and active optical phase control. The light source is focused into a fiber optic by lens 1. The source light travels through coupler 1 and coupler 2 to the scatter collection optics, which focus the light into the particle dispersion and collect light scattered from the particles as shown previously in this document. The scattered light, which travels back through the fiber optic, is split off by coupler 2 to detector 2, through coupler 4, and by coupler 1 to detector 1 through coupler 3. Source light is mixed with the scattered light through coupler 1 and coupler 3 for detector 1 and through coupler 2 and coupler 4 for detector 2. This source light provides the local oscillator for heterodyne detection on both detectors. An optical phase shifter (such as a piezo-electric fiber optic stretcher) is placed between coupler 2 and coupler 4 to control the optical phase of the local oscillator for detector 2 through a feedback loop, which continually maintains the phase difference between detector 1 and detector 2 signals as shown previously:

$$A_1 - A_2 = m\pi \quad \text{where } m \text{ is an odd integer}$$

The heterodyne signals from the two detectors are bandpass filtered, by BPF1, to only pass the frequencies of interest and  $F_{\text{mod}}$  (see below). In addition, the signal from detector 2 has adjustable gain  $G$  to balance the two signals as shown previously:

$$G = T_2/T_1$$

Both of the processed detector signals are subtracted by the DIFF difference circuit to produce the  $\Delta S$  signal as described previously. The detection system may need to maintain



the proper phase difference during periods when particles and scattered light are not present, to be ready for a particle transition. In this case, a phase modulator is placed between coupler 2 and the scatter collection optics to modulate the optical phase of the scattered light with very small optical phase deviation. The frequency,  $F_{mod}$ , of this modulation is outside of the light scatter heterodyne frequencies of interest, to avoid contamination of the particle characterization signal. A feedback loop controls the phase shifter, between coupler 2 and coupler 4, to continually maximize the  $F_{mod}$  frequency component in the  $\Delta S$  signal, accommodating thermal and stress induced optical phase drift in the fiber optics. The  $\Delta S$  signal is filtered, by bandpass filter BPF3, to remove spurious signals and to pass only the  $F_{mod}$  frequency component to the feedback controller. The  $\Delta S$  signal is filtered, by bandpass filter BPF2, to pass the scatter signals of interest and to remove the  $F_{mod}$  frequency component before being digitized for analysis by the computer. If particles are present continuously or for sufficient period to adjust the optical phase before data collection, then the feedback circuit could control by maximizing the scatter portion of the heterodyne signal, without the need for the optical phase modulator at  $F_{mod}$ . The same methods, as described previously using anti-reflection coatings and beam dumps, should be used to reduce the light reflection at all ends of fiber optics and surfaces of conventional optics to avoid laser feedback noise and interferometric noise. Figure B5 shows details of the fiber terminator, in Figure B4, which reduces light reflection back into the end of the fiber optic, due to Fresnel reflection at the fiber/air interface. A thick optical window, with refractive index which nearly matches the index of the fiber optic core, is attached to the fiber end with adhesive or gel which also nearly matches the fiber optic core refractive index. The back reflection is reduced substantially because the air/window reflecting surface is anti-reflection coated and that surface is moved far from the entrance to the fiber optic core. This anti-reflecting surface could also be tilted to direct the reflected beam away from the fiber optic core. In either case, the back reflected diverging beam has extremely low intensity at the fiber optic core.

The system in Figure B4 could be utilized in any dynamic scattering system by designing the BPF1 and BPF2 filters to pass the frequencies of interest for the particular application. This includes measurement of Brownian motion broadened scatter spectrum to determine particle size or the flow tube particle detector described previously. The system shown in Figure B4 (and in Figure B3) could replace the detection system in Figure B2, by placing the end of the fiber optic, which interfaces with the scatter collection optics in Figure B4, at the position of aperture 3 in Figure B2, to project a light beam down the tube and to collect scattered light from any particle in the tube, through lens 6. The system in Figure B4 could also be designed as an integrated optic chip to reduce production costs.

These techniques could be applied to remove excess laser noise from any heterodyne signals.

### **Zeta Potential**

The Zeta potential of particles can be determined from the electric mobility, of the particle, measured from the particle velocity in an electric field. However, motion of the dispersing fluid in the electric field can produce errors in the measurement of the particle motion. One way of reducing the fluid motion is to use an oscillating electric field, which rapidly oscillates positive and negative as shown in Figure C1. Then the dispersing liquid cannot react as quickly as the particles, and the fluid motion is reduced significantly. Figure C1 also shows the particle velocity due to this oscillating field. This motion can be measured by sensing the Doppler shift of light scattered by the moving particles. Since the particles cannot react immediately to the changes in the electric field, the particle velocity should be sensed over a reduced section of each cycle where the velocity has reached a stable value, as indicated by the analog to digital converter switch function shown in Figure C1. When the switch is high the analog to digital converter (A/D) collects samples of the signal from the scattering detectors, shown in Figures C2 and C3. Likewise, the

analog to digital converter (A/D) can also digitize signal during the corresponding segments of the negative electric field pulses and the same analysis applied to that data. The reduced A/D collection period is chosen to measure only while the particle velocity is nearly constant. If the A/D period is longer, the spectrum of the signal can be corrected for the resulting spectral broadening by including the shape of the velocity function in calculation of  $W(f)$  ( $W(f)$  would be the power spectrum of the actual velocity vs. time function instead of the RECT function, see below).

Figures C2 and C3 show two configurations for a fiber optic system which uses heterodyne detection to measure the spectrum of light scattered by the moving particles. In Figure C2 the local oscillator is provided by reflection from port 3 (back through the fiber optic coupler to the detector); and in Figure C3 the local oscillator is provided directly from port 3 to the detector. In each case the scattered light is mixed with light from the optical light source to produce a beat frequency spectrum indicative of the particle motion due to the electric field and Brownian motion. The electric field should be nearly parallel to the optical axis of the scatter collection optics to maximize the Doppler frequency. This can be accomplished by placing two electrodes in the particle dispersion, with a transparent electrode closest to the scatter optics. Since the particle charge can be positive or negative, the particle velocity and Doppler shift can be positive or negative. Therefore, the spectrum of the heterodyne signal should be upshifted to be centered about some frequency which is greater than the largest negative Doppler frequency shift which is to be detected. This frequency upshift can be provided by optical phase modulation of the source light, just before the light is mixed with the scattered light, to provide a frequency shift to the entire spectrum. If the optical phase is ramped during the data collection, as shown in Figure C1, the spectrum of the scatter detector current will be upshifted, so that both positive and negative sides of the spectrum can be seen. The optical phase shifter could also be replaced by an acousto-optic frequency shifter.

The power spectrum  $P(f)$  of the detector current, from data taken during the A/D sample period, in either configuration will consist of the Doppler spectrum,  $S(f)$ , from the particle motion due to the electric field force on the particles, convolved with the Doppler spectrum,  $B(f)$ , due to Brownian motion and the spectral broadening,  $W(f)$ , due to the finite width or shape of the velocity vs. time function.

$$P(f) = S(f) \otimes B(f) \otimes W(f)$$

Where  $\otimes$  is the convolution operator

The goal is to determine  $S(f)$  which is indicative of the motion due to the electric field force. This can be solved for by inverting the  $P(f)$  equation using deconvolution algorithms where the impulse response for the algorithm is:

$$H(f) = B(f) \otimes W(f)$$

For example, if the velocity is constant during the A/D sampling period,  $W(f)$  is the square of the SINC function ( $\sin(x)/x$ ) from the Fourier Transform of the RECT (rectangle) function representing the A/D sampling period. Use of this function is optional;  $W(f)$  could be eliminated from the above equations, but with additional spectral broadening in the result for  $S(f)$ .  $B(f)$  is the Lorentzian function which describes the spectral broadening due to Brownian motion of the particles. So these two spectral broadening mechanisms can be removed from  $P(f)$  to produce the spectrum,  $S(f)$ , due to only the particle motion caused by the electric field force on the particles, by using deconvolution algorithms such as iterative deconvolution. This deconvolution could be done multiple times over various frequency intervals for  $P(f)$ , where each interval represents the region for a particular size of particles, because  $B(f)$  is particle size dependent. Therefore the various modes in the  $S(f)$  function should each be associated with a certain particle diameter,  $d$ , and a certain Brownian spectral broadening  $B(d,f)$ . Each of these frequency intervals could be deconvolved individually, using the  $B(d,f)$  corresponding to the size of the particles in that interval. Otherwise, if this correspondence is not known, the entire spectrum could be deconvolved with the

$B(d,f)$  for either the average particle diameter  $d$ , or the largest particle diameter  $d$  of the particle sample. The solution, based upon the largest  $d$ , would provide the least amount of spectral sharpening and mobility resolution, but it would not produce artifacts from "over-sharpening" of the spectra, which would be caused by using  $B(d,f)$  from a diameter  $d$  which is smaller than most of the particles in the sample. The size of the particles can be determined by turning off the electric field and measuring the Brownian broadened spectra alone and using known methods to determine the size distribution from the power spectrum. This measured Brownian spectrum (with electric field off) could also be used directly for  $B(f)$  in the deconvolution of the entire spectrum  $P(f)$ ; or individual modes of the Brownian spectrum,  $B(f)$ , could be associated with certain modes of  $P(f)$  to break  $P(f)$  up into multiple frequency ranges (one for each mode) with a separate deconvolution and separate  $B(f)$  function for each deconvolution. The measured Brownian spectrum with zero electric field is the positive frequency half of the full symmetrical Brownian spectrum, which is symmetrical about zero frequency. Therefore,  $B(f)$  is created by using the measured Brownian spectrum for positive frequencies only and using the mirror image of that spectrum for the negative frequency region, producing a full function  $B(f)$ , which is symmetrical about zero frequency, from the positive frequency half spectrum provided by the measured Brownian spectrum at zero electric field.

If  $P(f)$  were measured at various peak electric field values, the Brownian spectral broadening could be determined for each mode in  $S(f)$ . As the electric field increases, the frequency scale of each mode in  $S(f)$  will expand proportionally, but  $B(f)$  is independent of electric field. At very high electric fields, the modes in  $S(f)$  will be well separated, but  $B(f)$  will be the same. Therefore, a set of simultaneous equations, for  $P(f)$ , can be set up to solve for the  $S(f)$  portion of  $P(f)$ :

$$P(f, E1) = S(f, E1) \otimes B(f) \otimes W(f)$$

$$P(f, E2) = S(f, E2) \otimes B(f) \otimes W(f)$$

$$P(f, E3) = S(f, E3) \otimes B(f) \otimes W(f)$$

This set is for 3 different values of electric field,  $E_1$ ,  $E_2$ , and  $E_3$ . But any number of equations can be formed by measuring at more values of electric field  $E$ .  $W(f)$  is known from the A/D switch function and velocity function.  $B(f)$  can be determined by deconvolving all simultaneous equations with one of many different trial functions of  $B(f)$ . Only the true  $B(f)$  function will produce the same frequency scaled solution  $S(f, E)$  for each of the equations, where frequency scaled solution  $S(f, E)$  is given by:

$$S(f, E) = S(f \cdot E_1/E, E_1) \text{ for the } P(f, E_1) \text{ equation}$$

$$S(f, E) = S(f \cdot E_2/E, E_2) \text{ for the } P(f, E_2) \text{ equation}$$

$$S(f, E) = S(f \cdot E_3/E, E_3) \text{ for the } P(f, E_3) \text{ equation}$$

The value of  $S(f)$  at each value of  $f$  is proportional to the scattered light of the particles with the velocity and corresponding Doppler shift equal to  $f$ . Therefore, the number or volume of particles at that velocity can be calculated by dividing  $S(f)$  by the appropriate scattering efficiency for the particles of corresponding size, which is calculated from the Brownian broadening for that particular mode in  $S(f)$ . In any case, once  $S(f)$  is determined, the particle number vs. particle velocity distribution, particle number vs. mobility distribution, and particle number vs. Zeta potential distribution can all be determined directly from  $S(f)$ , because the particle velocity is proportional to frequency  $f$  with known constant of proportionality; and the mobility and Zeta potential can be calculated from the velocity using known relationships. The above analysis can be applied to  $P(f)$  calculated from the data collected during each A/D sample period in Figure C1, or it can be applied to the power spectrum of the concatenation of the detector signal data sets from multiple A/D periods. Also, the detector current power spectra functions from multiple A/D periods can be averaged to produce a final averaged  $P(f)$  which becomes the input  $P(f)$  for the analysis described above.

Measurement at low scattering angles is desirable for mobility measurement of particles to reduce the Doppler broadening due to

Brownian motion. However, large particles scatter much more light at small angles than small particles do; and so the scatter from any debris in the sample will swamp the Doppler signal from the electric field induced motion of the smaller charged particles in the electric field and cause errors in the Zeta potential measurement. Figure C4 shows a method of measuring Dynamic light scattering from a small interaction volume created by restricting the size of the illuminating beam and the effective viewing volume. When only scattered light from a very small sample volume is measured, the scatter signal from large dust particles will be very intermittent, due to their small count per unit volume. The data sorting techniques outlined by this inventor previously, in "Methods and Apparatus for Determining the Size and Shape of Particles", can be used to eliminate the portions of the signal vs. time record which contain large signal bursts due to passage of a large particle. The system shown in Figure C4 can also be used with those same data sorting techniques to sort and group data sets with different characteristics before final inversion to determine the particle size distribution, because the small viewing volume increases the signal change and discrimination during the passage of a large particle. And in the Zeta potential case, measurements can be made at low scattering angles without the scattering interference from dust contaminants, because the signal vs. time segments, which are contaminated by large particle signals, can be eliminated from the data set which is analyzed for mobility measurements.

The spectral power in certain frequency bands, as measured by fast Fourier transform of the data set or by analog electronic bandpass filters, could be used to categorize data sets. Also the ratio of scattering signals at two scattering angles would indicate the size of the particles. Consider a Zeta potential measuring dynamic scattering system (for example as shown in Figure C4) where the scattering signal from the detector is digitized by an analog to digital converter for presentation to a computer algorithm. The entire data record is broken up into shorter data sets. In addition, the signal could be connected to analog filters and RMS circuits, which are sequentially sampled by the analog to digital converter to append each digitized data set with values of total power in certain appropriate frequency

bands and at certain scattering angles which provide optimal discrimination for larger particles. The use of analog filters may shorten the characterization process when compared to the computation of the Fourier transform. These frequency band power values are then used to sort the data sets into groups of similar characteristics. Since larger particles will usually produce a large signal pulse, both signal amplitude and frequency characteristics can be used to sort the data sets. A large peak signal value in any data set would also indicate the presence of a large particle in that set.

The use of analog filters is only critical when the computer speed is not sufficient to calculate the power spectrum of each data set. Otherwise the power spectra could be calculated from each data set first, and then the power values in appropriate frequency bands, as determined from the computed power spectrum, could be used to sort the spectra into groups before the data is processed to produce velocity and mobility distribution. Data sets, with very high signal levels at low scattering angles and low signal levels at high scattering angles, could also indicate the presence of large particles and debris. Or a simple signal level threshold could be used to reject data sets with large signal pulses due to debris. These large particle or debris data sets, as selected by the various criteria outlined above, are not included in the final power spectrum which is used to calculate the particle velocity, mobility, and Zeta potential distributions.

The system in Figure C4 shows two detectors: detector 1 measures backscatter for size and mobility measurements (primarily for size due to large Brownian component) and detector 2 measures forward scatter for size and mobility measurements (primarily for mobility due to small Brownian component). The fiber optic coupler provides the local oscillator for heterodyne detection, using a phase modulator as used in Figures C2 and C3. The beamsplitter mixes the phase modulated local oscillator light with the scattered light onto detector 2. Lens 2 and the pinhole at detector 2 define a small viewing volume. The intersection of this restricted viewing volume with the focal spot of the source beam from lens 1 defines a small scatter interaction volume, where the average count of larger debris particles is much less



than one. The light rays, passing through lens 1, represent light from the source and the rays, passing through the beamsplitter and lens 2, represent scattered light. An electric potential is placed across the two plate electrodes, in Figure C4, to produce the electric field to induce the charged particle motion. A partial reflector before lens 1 provides the local oscillator for detector 1. However, the Fresnel reflection at the fiber optic port 4 should be sufficient to provide the local oscillator for detector 1, without the partial reflector. The optical phase modulator can be a fiber optic phase modulator, which are inexpensive to manufacture. Other heterodyne system designs, with small interaction volumes, can be used to make this measurement as shown previously by the inventor in "Methods and Apparatus for Determining the Size and shape of Particles". By replacing the flow cell with a non-flowing cell with electrodes, the same techniques can be employed using those designs.

#### **Methods and apparatus for determining particle size distribution by measuring scattered light and using centrifugation or settling**

Many particle size measuring systems measure the light scattered from an ensemble of particles. Unfortunately these systems cannot measure mixtures of large and small particles, because the scattering efficiency (the scattered intensity at a certain scattering angle per particle per incident intensity) of the smaller particles is much less than that of the larger particles. The contribution of scattered light from the smaller particles is lost in the more intense scattering distribution from the larger particles. These particle ensemble measuring systems also cannot resolve two closely spaced modes of a volume-vs.-size distribution or detect a tail of small particles in the presence of larger particles. This is true for both static (angular scattering) and dynamic (power spectrum or autocorrelation of the scattered light detector current) scattering distributions which must be inverted to determine the particle size distribution. This section describes methods and apparatus for centrifugal size separation and spatial separation

of the particles, for subsequent spatial evaluation by either static or dynamic light scattering.

Particles in a centrifugal force field accelerate in the fluid until the viscous drag and centrifugal force is balanced. This velocity is the terminal velocity of the particle. To first order, this velocity is proportional to the product of the differential density of the particle to the surrounding liquid, the centrifugal acceleration, and the square of the particle diameter. If an ensemble of particles of various sizes is placed into a centrifugal force field, each size will reach a different terminal velocity and travel a different distance, in the direction of the centrifugal force, in a given time period. So the particles will spread out or become redistributed spatially according to size. This spatial distribution is then scanned by either a static or dynamic scattering system to accurately determine the particle size distribution. This idea could be implemented with dedicated optical scattering detection hardware or could be added as a sample cell accessory to existing particle size instruments.

The first step of the process is illustrated in Figure D1. A sample cell, which has two optical windows, is filled with clean dispersant. The concentrated particle dispersion is introduced at the top of sample cell and capped. This cell is then placed into a standard centrifuge for centrifugation for a predetermined period of time. The sample cell may be designed to fit into a standard slot in a centrifuge rotor or a custom rotor may be designed to hold the sample cell (or cells). Many cells could be centrifuged at one time.

This technique will work with any starting distribution of the particles before centrifugation. Because size dependent separation will always occur, leaving smaller slower particles separated closer to their starting point, the smaller particle's size and concentration can be measured separately from the larger particles. This separation eliminates or greatly reduces the scattering cross-talk between particles of various sizes and prevents the smaller particles from getting lost in the scattering distributions of the larger particles.

The optimal starting particle concentration distribution is shown in Figure D1 (see also Figure D4), with all particles in a layer close to the axis of rotation for the centrifuge. In this case each particle size mode will separate out into an individual band of particles in the sample cell, during centrifugation. So a tri-modal size distribution (see Figure D4) would produce three spatially separate bands along the direction X of the centrifugal force. In the case of a broad size distribution, the various size particles might be distributed along the X direction as shown in Figure D2 (concentration distribution not shown).

After centrifugation, the sample cell is removed from the centrifuge and inserted into a scattering instrument as shown in Figure D3, for the case of static scattering. The static scattering optical system measures the light scattered at various angles. The light source is collimated or focused (to interrogate smaller portions of the sample cell for higher spatial resolution) by lens 1. The resulting light beam passes through the sample cell and is scattered by the particles. The scattered light and the unscattered beam are focused onto an array of detectors in the back focal plane of lens 2. A larger scattering angular range may be obtained by using multiple lens/array units or by using multiple light sources. The sample cell is scanned in the direction of the centrifugal force to measure the scattering distribution at various X positions. Many existing angular scattering methods can also be used to scan the cell and determine the particle size distribution at each X position. The cell and motorized stage could also be placed into commercially available dynamic or angular scattering instruments to scan the cell. Each detector element measures the light scattered over the angular range defined by that element. The resulting intensity-vs.-scattering angle distribution is inverted to obtain the particle size distribution. This is usually accomplished by iterative methods such as iterative deconvolution or regression. Also certain size parameters may be determined from intensity measurements at only a few scattering angles which would reduce the time per inversion and the instrument cost. For example, consider the case where only 4 scattering angles are measured to determine the mean particle size at each position. The theoretical values for these 4

detectors vs. particle size may be placed in a lookup table. The 4 detector values from a measured unknown particle segment are compared against this table to find the two closest 4 detector signal groups, based upon least squares minimization. The true size is then determined by interpolation between these two best data sets based upon interpolation in 4 dimensional space. The theoretical values for these 4 detectors vs. particle size may be placed in a lookup table. The 4 detector values from a measured unknown particle are compared against this table to find the two closest 4 detector signal groups, based upon the least squares minimization of the functions such as:

$$(S1/S4-S1T/S4T)^2 + (S2/S4-S2T/S4T)^2 + (S3/S4-S3T/S4T)^2$$

or

$$(S1/SS-S1T/SST)^2 + (S2/SS-S2T/SST)^2 + (S3/SS-S3T/SST)^2 + (S4/SS-S4T/SST)^2$$

where

$$SS = S1 + S2 + S3 + S4$$

$$SST = S1T + S2T + S3T + S4T$$

where S1,S2,S3,S4 are signals from the 4 detectors, S1T,S2T,S3T,S4T are the theoretical values of the four signals for a particular particle size, and ^2 is the power of 2 or square of the quantity preceding the ^.

The true size is then determined by interpolation between these two best data sets based upon interpolation in 4 dimensional space. The look up table could also be replaced by an equation in all 4 detector signals, where particle size equals a function of the 4 detector signals. This disclosure claims the use of any number of detectors to determine the particle size, with the angles and parameterization functions chosen to minimize size sensitivity to particle composition.

In any case, these scattering measurements are made at various locations along the X direction (the direction of the centrifugal force) by moving the sample cell under computer control on a motorized stage. The intensity distribution is inverted at each location to calculate the size distribution of particles at that location. This computation is started by calculating the mean particle size at a few points (X values) along the cell. This size-vs.-X data provides an effective density for the particles, using the Stokes equation for centrifuge (equation 1a or equation 1) to solve for particle density viscosity ratio using the size vs. X values. This is accomplished by doing a regression analysis on either  $X = V \cdot t$  (using equation 1a) or  $X = R^2$  (using equation 1) vs. D to solve for  $(\rho_1 - \rho_2)/\eta$ . The K value (including the effects of viscosity) in equation 2 could also be determined. Then using this effective density viscosity ratio or K value, the expected size range of particles at each X location is calculated based upon the theoretical motion of the particles in the centrifugal force field for the given period of time. The scattering distribution at each location (static or dynamic) is then inverted with a constrained inversion algorithm which limits the solution range of particle size at each location to cover a range which is similar to, but larger than, the range of sizes expected to be resident at that location, based upon equation 1a or equation 1. This prevents the particle size solutions in regions of larger particles from containing smaller particles which could not have been present at the location of the larger particles. These erroneous smaller particles might result from errors in the scattering model for high angle scattering from the larger particles. This high angle scattering tail for larger particles can change with particle refractive index and particle shape, and so it may not be known accurately. Therefore if small particles are allowed in a particle size solution for a region which should only have large particles, errors in the particle composition or high angle scattering measurements could cause the inversion algorithm to report small particles which are not real. The particle size distributions from these various locations are combined into one continuous distribution by adding them together as relative particle volume (relative among X locations) using the scattering efficiency (intensity per unit

particle volume) of each particle size to calculate the particle volume at each location from the scatter intensity at that location.

The static scattering system could also be replaced by a dynamic scattering system as shown in Figure D3B. Other dynamic light systems which could be used in this configuration were described previously in this document. Replace the cuvette, in those systems, with the centrifuge cell and motorized stage in Figure D3B. To determine the particle size distribution, either the autocorrelation function or power spectrum of the detector current is inverted to create the particle size distribution at each point in the cell. Dynamic light scattering has been used to measure particle size by sensing the Brownian motion of particles. Since the Brownian motion velocities are higher for smaller particles, the Doppler broadening of the scattered light is size dependent. Both heterodyne and homodyne methods have been employed to create interference between light scattered from each particle and either the incident light beam (heterodyne) or light scattered from the other particles (homodyne) of the particle ensemble. Heterodyne detection provides much higher signal to noise due to the mixing of the scattered light with the high intensity light from the source which illuminates the particles.

In Figure D3B a light source is focused through a pinhole by lens 1 to remove spatial defects in the source beam. The focused beam is recollimated by lens 2 which projects the beam through an appropriate beamsplitter (plate, cube, etc.). The diverging light source, lens 1, pinhole 1, and lens 2 could all be replaced by an approximately collimated beam, as produced by certain lasers. This nearly collimated beam is focused by lens 3 into the particle dispersion which is contained in the centrifuge cell or container with a window to pass the beam. The focused beam illuminates particles in the dispersion and light scattered by the particles passes back through the window and lens 3 to be reflected by the beamsplitter through lens 4 and pinhole 2 to a detector. A portion of the incident collimated source beam is reflected from the beamsplitter towards a mirror, which reflects the source light back through the beamsplitter and through the same lens 4 and pinhole 2 to be mixed with the

scattered light on the detector. This source light provides the local oscillator for heterodyne detection of the scattered light from the particles. The mirror position must be adjusted to match (to within the coherence length of the source) the optical pathlengths traveled by the source light and the scattered light. This is accomplished by approximately matching the optical path length from the beam splitter to the scattering particles and from the beam splitter to the mirror. The interference between scattered and source light indicates the velocity and size of the particles. The visibility of this interference is maintained by pinhole 2 which improves the spatial coherence on the detector. Pinhole 2 and the aperture of lens 3 restrict the range of scattering angle (the angle between the incident beam and the scattered light direction) to an angular range approximately 180 degrees. Multiple scattering can be reduced by moving the focus of lens 3 to be close to the inner surface (the interface of the dispersion and the window) of the sample cell window. Then each scattered ray will encounter very few other particles before reaching the inner window surface. Particles far from the window will show multiple scattering, but they will contribute less to the scattered light because pinhole 2 restricts the acceptance aperture. Multiple scattering is reduced as long as the short distance of inner window surface to the focal point (in the dispersion) of lens 3 is maintained by appropriate position registration of the cuvette.

This design can provide very high numerical aperture at the sample cell, which improves signal to noise, reduces multiple scattering, and reduces Mie resonances in the scattering function. Light polarization is also preserved, maximizing the interference visibility.

The sample cell (after centrifugation) is moved by a motorized stage so that the interaction volume of the scattering system is scanned along the length (x direction) of the cell. The stage stops at various positions to accumulate a digitized time record of the detector current. The time record at each position is analyzed to determine the particle size distribution at that position. Usually either the power spectrum or autocorrelation function of the detector current vs. time record is inverted to produce the particle size distribution at each X position. This

inversion may be constrained, as described above. These size distributions at various X positions are combined together to produce the complete distribution as described previously and in more detail later.

This process can be used with any starting concentration distribution. For example, if the starting distribution is homogeneous throughout the entire sample cell before centrifugation (see Figure D5), then after centrifugation the low X region will only contain small particles because the faster larger particles have left that region. From the relative volume in each region (calculated from the theoretical scattering efficiency) and the theoretical concentration distribution vs. X for each particle size (calculated from the X position, the effective particle density, and theoretical terminal velocity for each size), the total volume of each particle size can be calculated over the entire cell. These total volume values are then combined to generate the particle volume-vs.-size distribution for the entire sample.

The terminal velocity V in a gravitational field is given by (see parameter definitions below):

$$(1a) \quad V = 2g(D^2)(p_1 - p_2)/(9\eta) \quad \text{for gravitational acceleration } g$$

So the distance traveled by the particle in time t is simply  $V \cdot t$ .

In order to understand the analysis of the resulting dispersion in a centrifuge, one must determine how the particles move within a centrifugal force field. A particle at radius R1 at time t=0 will move to radius R2 at time t, where R1 and R2 are radii measured from the center of rotation of the centrifuge. These parameters are determined by the modified Stokes equation (equation 1b) for particles in a centrifugal force field.

$$(1b) \quad \ln(R_2/R_1) = 2(\omega^2)(p_1 - p_2)(D^2)t/(9\eta)$$

where



w is the rotational speed of the centrifuge in radians per second

p1 is the density of the particle

p2 is the density of the dispersant

q is the viscosity of the dispersant

t is the duration of centrifugation

D is the particle equivalent Stokes diameter (hydrodynamic diameter)

^ is the power operator

ln is the natural logarithm operator

We may rewrite this equation in the following form:

$$(2b) \quad \ln(R2/R1) = K(D^2)$$

$$\text{where } K = 2(w^2)(p1-p2)t/(9q)$$

Particles at larger radii R1 will move farther due to the higher centrifugal acceleration at the larger radius. Therefore, the concentration of particles will decrease during the centrifugation process, because, for a given particle size, the particles at larger radii will travel faster. However, if the separation is accomplished by settling in a gravitational field, then the concentration is constant in the regions which still contain particles after settling. These regions would be particle size dependent because faster settling particles will reside closer to the bottom of the sample cell. Therefore, in any region where a certain size particle resides, the concentration of that particle size should be nearly constant over that region for gravitational settling.

But first consider the centrifugal case. For any infinitesimal segment of the dispersion, the concentration will follow equation 3b.

$$(3b) \quad C1 \cdot \Delta R1 = C2 \cdot \Delta R2$$

where  $\Delta R1$  is the length of the segment at  $t=0$  and  $R = R1$

and  $\Delta R2$  is the length of the same segment at  $t=t$  and  $R = R2$

If we let  $Z = \ln(R)$ , then  $\Delta R = R\Delta Z$  and

$$(4b) \quad C_1 R_1 \Delta Z_1 = C_2 R_2 \Delta Z_2$$

If the starting segment is between  $Z_{11}$  to  $Z_{12}$  at  $t=0$ ; and the same segment fills the region between  $Z_{21}$  and  $Z_{22}$  at  $t=t$ . Then using equation 2b we obtain:

$$(5b) \quad Z_{21} - Z_{11} = k(D^2)$$

$$(6b) \quad Z_{22} - Z_{12} = k(D^2)$$

$$(7b) \quad \Delta Z_1 = Z_{12} - Z_{11}$$

$$(8b) \quad \Delta Z_2 = Z_{22} - Z_{21}$$

From equations 5b, 6b, 7b, and 8b we obtain:

$$(9b) \quad \Delta Z_1 = \Delta Z_2$$

$$(10b) \quad C_1 R_1 = C_2 R_2$$

$$(11b) \quad C_2 = C_1 \exp(-K(D^2))$$

where  $\exp$  is the exponential function.

So any small segment of the dispersion at centrifugal radius  $R_1$  will move to radius  $R_2$  under the centrifugal force and change concentration from  $C_1$  to  $C_2$ . Therefore, the particle concentrations measured at various  $R$  values must be corrected for the change in concentration from the original starting distribution. For the case where all of the particles start close to  $R_1$  as shown in Figure D4, the measured concentration at  $R_2$  can be multiplied by  $R_2/R_1$  to correct the concentration back to the starting concentration or the concentration can simply be multiplied by  $R_2$  before normalization for a concentration-vs.-size distribution (or volume percent vs. size). In the second case shown in figure D5, where the particles are uniformly dispersed throughout the sample cell at  $t=0$ , the concentration

for each size is lowered by a factor of  $\text{EXP}(-K(D^2))$  through out the cell volume where those particles reside. For the case of settling in a gravitational field (gravitational force along the R direction), which may be used for samples with high settling velocities, the concentrations remain the same during the settling process and no corrections are required in regions where all of the particles of each size are present. After a time, the larger particles will leave the region of lowest R value and the concentration of that largest size will drop in that region.

The detection process consists of measuring the angular light scattering data set for static scattering, or the power spectrum (or autocorrelation function) data set for dynamic scattering, at various values of R along the sample cell after centrifugation or settling. These data sets at each value of R will be described by  $F_{jm}$  for the jth element of the mth data set at  $R=R_m$ .

Dataset element  $F_{jm}$  is the jth element of the mth dataset collected at radius  $R_m$ . The index m increases with increasing centrifugal radius or increasing settling distance (in the gravitational case). Larger or denser particles will reside at larger values of m. The dataset can consist of any data collected to determine the particle size, such as scattered flux at the jth scattering angle, dynamic scattering detector power in the jth spectral band, or dynamic scattering autocorrelation function in the jth delay ( $\tau$ ). Any of these data values represent the net data values after background has been subtracted. The background is measured by collecting the data with no particles in the laser path at each value of R. Each data set is corrected for the incident intensity of the scattering source. Each static scattered data set is divided by the source intensity; and each power spectrum or autocorrelation function is divided by the square of the source intensity. So all values of  $F_{jm}$  are normalized to the equivalent signal for unit incident intensity, for both static or dynamic light scattering.

$V_{ik}$  is the ith element of the kth particle volume-vs.-size distribution.  $D_i$  is center diameter of the ith particle size

channel of this volume-vs.-size distribution (the total particle volume in each particle diameter bin). This volume-vs.-size distribution can be converted to particle number-vs.-size or particle area-vs.-size by known techniques.

Definition: The sum of elements of vector Y,  $Y_i$  from  $i=m$  to  $i=n$  is defined as:

$$\text{SUM } i:m:n (Y_i)$$

Then let the function  $L = LX(n1, n2, n3, n4)$  be defined as:

$$S1_j = \text{SUM } m:n1:n2 (F_{jm})$$

$$S2_j = \text{SUM } m:n3:n4 (F_{jm})$$

$$L = \text{SUM } j:1:j_{\max} (((S2_j / (\text{SUM } j:1:j_{\max} (S2_j))) - ((S1_j / (\text{SUM } j:1:j_{\max} (S1_j)))^2)$$

$j_{\max}$  =max value of  $j$  and  $m_{\max}$  =maximum value of  $m$

The purpose of function LX is to compare the current data set (or sum of the last few data sets) to a prior (or sum of a few prior data sets) to determine if the size distribution has changed significantly, prompting the next calculation of  $V_{ik}$ . This will be described more clearly in the next section.

### **Starting with a layer of particles at low R value**

The first method involves starting the centrifugation or gravitational settling process with all of the particles in a narrow R region at the low R end of the cell as shown in Figure D4 (or at the top of the vertical oriented cell in the case of gravitational settling). This method will be described in more detail in Figures D7a and D7b. After centrifugation or settling, particles with different terminal velocities will arrive at different centrifugal radii or X values (see figures D3 and D4). The light beam in figure D3 should be shaped to provide a nearly rectangular intensity profile (flat top profile) in the X direction. The motorized stage would then move in steps of distance equal to (or less than) the X width of this rectangular intensity profile so as to sample the entire cell with some

minimal overlap between beam samplings of the particle dispersion. At each step, the scattering data is inverted to produce the size distribution (particle volume-vs.-particle diameter or size) for the particles in the beam at that step. The scattering system can usually be modeled as a linear system:

$$F = H*V$$

Where F is the vector of measured scatter values (angular scattering vs. angle, power spectrum vs. frequency, or autocorrelation function vs. delay). Element F<sub>j</sub> could be the scattered flux at the jth scattering angle, the dynamic scattering detector power in the jth spectral band, or the dynamic scattering autocorrelation function in the jth delay (tau). V is the particle volume-vs.-size distribution vector, the particle volume in each size bin. H is the theoretical model matrix for the particles. Each column in H is the F response for the corresponding size of the matrix multiplying element from the V vector. This model depends upon the refractive indices of the particles and the dispersant. This matrix equation can be solved for V at each R (or X) value; or certain parameters (such as mean diameter and standard deviation) of the size distribution could be determined using the search methods described above. In either case, the volume distribution at each X value must be scaled before being combined. Usually the volume, calculated by solving F=H\*V for V or by using the lookup tables, is normalized to a sum of 1.0 (i.e. 100%). This normalized volume, V<sub>n</sub>, must be scaled before being added to the volume distributions from other R values to produce the complete volume distribution, V<sub>i</sub>. This is accomplished by first calculating the normalized F<sub>n</sub>:

First calculate the vector  $F_n = H*V_n$

Taking the measured data vector F<sub>m</sub>, which produced V<sub>n</sub>, calculate the value P by computing either:

$$P = (\text{SUM } i:1:\text{imax } (F_{mi}/F_{ni})) \quad \text{or}$$

$$P = ((\text{SUM } i:1:\text{imax } (F_{mi})) / (\text{SUM } i:1:\text{imax } (F_{ni})))$$

Each size distribution is corrected for the scattering efficiency and theoretical centrifugal concentration change from the starting dispersion,  $(\text{EXP}(-K(D^2)))$ , to produce an absolute total particle volume measurement or at least one that is properly related to the other distributions measured at other values of  $R$ . The  $\text{EXP}(-K(D^2))$  concentration correction is not required for the case of particle settling. The inversion at each value of  $R_k$  could be constrained to only solve for particle sizes that are expected to be in the range of  $R$  at that step, as determined from using equation 1 or 1a with the computed effective particle density viscosity ratio or  $K$  value. The solution could also be constrained to a certain size range centered on the peak of the full size distribution calculated from that data set. This peak size could also be estimated from the flux distribution with a polynomial equation of the scattering model, to save computation time. The final values of the constrained particle volume,  $V_{ik}$ , calculated at the  $k$ th value of  $R_k$  for diameter  $D_i$ , are summed together (over the various  $k$  values) to produce the final volume distribution:

$V_i = \text{SUM } k:1:k_{\text{max}} (P_k * V_{ik} * \text{EXP}(K(D_i^2)))$  for centrifugal force

$V_i = \text{SUM } k:1:k_{\text{max}} (P_k * V_{ik})$  for settling

(Note:  $k$  is an index and  $K$  is a constant, and  $V_i$  is the particle volume in the size bin whose center is at particle diameter  $D_i$ )

### **Starting with a nearly homogeneous concentration distribution of particles over the entire cell**

Another easier starting distribution is simply to fill the entire cell with the particle dispersion before centrifugation or settling. The downside is that the different particle sizes are not separated into bands for each size as shown in figure D4. The particle concentration distribution for the homogeneous start is shown in Figure D5. All particles of a single terminal

velocity (or hydrodynamic diameter) with the same starting point will move the same distance during centrifugation or settling. However, in the case of centrifugation, the force on each particle increases as the particle moves to larger centrifugal radius  $R$ , as shown by equation 1. So the starting concentration  $C_1$  (before centrifugation), for particles of hydrodynamic diameter  $D$ , will be lowered to concentration  $C_2$  after centrifugation as described by equation 11b. This effect is shown in Figure D5. The starting dispersion is a homogeneous mixture of particles of three different diameters,  $D_1$ ,  $D_2$ , and  $D_3$ . Equation 11b shows that after centrifugation the concentration for each size will decrease by a factor of  $\text{EXP}(-K(D^2))$ . This is due to the fact that particles that leave a certain section of the cell will be replaced by other particles which move into it. However, at the low  $R$  end of the cell, no particles will replace the particles which move out of that region. Hence there will be boundaries, as shown in Figure D5, below which no particles of a certain hydrodynamic size will reside, except by means of diffusion. Starting at the lowest  $R_k$  value, only the smallest particles in the original distribution will be measured. As the scattering detection beam moves to larger  $R$  values (by moving the cell along the  $X$  direction), more of the complete distribution will be measured but with lowered concentration as given by equation 11b. This process will easily measure smaller particles which will be separated out at the lower  $R$  values. This presents a problem for the simple inversion process as was described previously for use with the layer start (Figure D4), because at larger  $R$  values multiple sizes will reside together. The poor resolution of a simple inversion process may cause some errors in the size of the larger particles which are mixed with the smaller particles. The following method reduces these errors:

- 1) starting at the lowest  $R$  value and progressing to larger  $R$  values, measure the first flux distribution with significant signal levels  $F_{jn1}$  (at  $R_m$  with  $m=n1$ ) and calculate the size distribution  $V_{i1}$  from  $F_{jn1}$ . Each size distribution is corrected for the scattering efficiency, the scattered intensity, and  $\text{EXP}(-K(D^2))$  to produce an absolute total particle volume measurement or one that is properly related to the other distributions measured at other values of  $R$ . The  $\text{EXP}(-K(D^2))$

concentration correction is not required for the case of particle settling. Continue stepping to larger  $R_m$  values and measuring  $F_{im}$ , calculating the value  $L_1$  at each  $R_m$  until  $L_1$  becomes larger than some limit  $L_t$  at  $R_{n2}$ . At this point the scattered data has changed sufficiently to indicate that new particle sizes are present.

$$Q_j = (((F_{jm} / (\text{SUM } j:1:j_{\max} (F_{jm})) - (F_{jn1} / (\text{SUM } j:1:j_{\max}(F_{jn1})))^2)$$

$$L_1 = \text{SUM } j:1:j_{\max} (Q_j);$$

Invert the flux difference,  $F_j = F_{jn2} - F_{jn1}$ , to obtain the second volume distribution  $V_{i2}$ .

Starting at  $m=R_{n2}+1$  calculate  $L_2$  at each  $R_m$  until  $L_2$  becomes greater than  $L_t$  ( $F_{jn3}$  at  $R_{n3}$ ) then invert  $F_{jn3}-F_{jn2}$  to obtain  $V_{i3}$

$$Q_j = (((F_{jm} / (\text{SUM } j:1:j_{\max} (F_{jm})) - (F_{jn2} / (\text{SUM } j:1:j_{\max}(F_{jn2})))^2)$$

$$L_2 = \text{SUM } j:1:j_{\max} (Q_j);$$

Starting at  $m=R_{n3}+1$  calculate  $L_3$  at each  $R_m$  until  $L_3$  becomes greater than  $L_t$  ( $F_{jn4}$  at  $R_{n4}$ ) then invert  $F_{jn4}-F_{jn3}$  to obtain  $V_{i4}$

$$Q_j = (((F_{jm} / (\text{SUM } j:1:j_{\max} (F_{jm})) - (F_{jn3} / (\text{SUM } j:1:j_{\max}(F_{jn3})))^2)$$

$$L_3 = \text{SUM } j:1:j_{\max} (Q_j);$$

This cycle is continued until the end of the cell is reached at  $R_{m\max}$ . The volume-vs.-size distribution is calculated by summing all of the calculated  $V_{ik}$  over  $k$  as described previously.

$$V_i = \text{SUM } k:1:k_{\max} (P_k * V_{ik} * \text{EXP}(K(D_i^2))) \text{ for centrifugal}$$

$$V_i = \text{SUM } k:1:k_{\max} (P_k * V_{ik}) \text{ for settling}$$



This process provides two important advantages. The incremental flux is inverted at each inversion step to provide optimum accuracy and resolution. Inversions are only done when the incremental flux is significant to save computer time. However, inversions can be done at more values of  $R$ , if computer time is not an issue.

The strategies for both layer (slug) and homogeneous start are similar. The scattered signal (static or dynamic) is measured at the first radius where the signal to noise is satisfactory. The particle size distribution is calculated at this point from that data set (angular scattering distribution, or power spectrum or autocorrelation of the detector current) . Then the scattering detection system scan continues to next radius where the signal characteristics have changed significantly to indicate the presence of particles of a new size. At this point the sum of all of the data sets since the last particle size calculation are added together (for example, the signal at each scattering angle is summed over the data sets from various  $R$  values) and inverted to calculate the second size distribution, in the case of the layer start. This summation is done for each scattering angle (or power spectrum frequency band or autocorrelation delay) by summing over the data sets. In the case of the homogeneous start, the difference between this latest data set and the data set at the last size distribution calculation could be inverted to calculate the second size distribution. Then the first data set is replaced by the latest data set and the cycle is repeated until the end of the cell is reached. Each size distribution calculation (inversion) can be constrained to the expected size region covered by the accumulated set of signals since the last size distribution calculation. However, complete unconstrained inversions can also be used. For the constrained inversion, the constrained size range may be based upon some region around the peak size of the data set (or accumulated data sets for layer start), or the expected hydrodynamic size over that region of centrifugal radii, using equation 1 or 1a. These constraints can be the same for both the layer and homogeneous start, because in the homogeneous start the differential signal is inverted and this signal covers the same size range as in the layer case if the two endpoints are at the same radii. Essentially, in the layer method, all of the data sets are

summed by groups from certain regions where the particle size distribution does not change significantly. Each group sum is inverted to produce a size distribution. In the homogeneous method, the difference between the data sets, at the endpoints of each region of similar particle size, are inverted to produce a size distribution. Then the resulting size distributions are combined as shown before.

Computation time is saved by choosing groups of data, over which the size has changed less than a certain amount. If computation time is not a problem, the entire R range of the cell could be broken up into very small regions. The data sets in each region are summed to produce one data set which is analyzed to produce the particle size distribution in that region. Then the large number of size distributions from these regions are combined as described above in this disclosure. The most computationally intensive procedure is the inversion of the data to produce the size distribution. This procedure is usually an iterative algorithm or search algorithm to find the particle size distribution which produces a theoretical data set which has the best fit to the measured data set. So the number of regions should be minimized to save computation time. However, if the computer is very fast, the entire cell can be broken up into small segments of R and the particle size distribution can be generated for each of these small segments and then added together as described before without determining where the signal shape has changed significantly to indicate the presence of particles of a new size.

The following equations and Figure D6 provide another description of the data analysis process. Each signal is the sum of multiple data acquisitions at various values of X (different m indices). These values of m are spread over a narrow range of X (or R). Over this X range, the particle size does not change significantly. The sum of these data acquisitions lowers the noise and averages out the local particle concentration variations. These data sums,  $S_{in}$ , are compared to determine where the signal shape has changed significantly to indicate the presence of particles of a new size. This comparison is accomplished by comparing the difference of squares, DIFF, against a DIFF limit. When DIFF exceeds DIFF limit, the sum of

all of the signal sets since the last particle size calculation are added together (the signal at each scattering angle is summed over the data sets from various R values) and inverted to calculate the next size distribution in the case of the layer start.

$$S_{in} = \sum_{m:n1:n2} (F_{im})$$

$$DIFF(n,m) = \sum_{i:1:imax} ((S_{in}/(\sum_{i:1:imax}(S_{in})) - S_{im}/(\sum_{i:1:imax}(S_{im})))^2)$$

Figure D6 shows how different X (or R) regions are defined. The particle concentration, C, is plotted vs. X and DIFF is plotted vs. the dataset index j. At points b, c, and d, DIFF has exceeded the limit and all of the prior data sets in that region are summed to produce a single dataset which is inverted to create the particle size distribution in that region. In Figure D6, the sum of datasets between a and b produce the dataset for determining the particle size distribution in region 1. In the case of homogeneous start, the dataset at point a is subtracted from the dataset at the end point b to produce the data to be inverted for the particles of region 1.

When the system starts in the homogeneous case before centrifugation, the techniques are briefly listed below. These techniques assume that the first data set is collected at the minimum centrifugal radius and successive data sets are collected in sequence towards larger centrifugal radii.

- 1) Subtract the prior data from the present data and invert the difference to obtain the particle size distribution for that region. Then combine regions scaled by the absolute particle volume represented by each differential data set.

- 2) Constrain the present inversion to match the results of the inversion of data from the prior measured region in the primary size region of the prior region.

- 3) Invert all of the data sets from different regions, individually, and then combine them by using the size distribution in the primary size region of each data set and scaling them to each other in overlap size regions.

As you can see, the homogeneous method is the more difficult method for signal inversion because of the inaccuracies in the signal differences. However this method is the easiest to implement because you simply fill the cell with a homogeneous dispersion. In the case of the layer method, a thin layer of dispersion must be placed at the top of a cell filled with clear dispersant. A method for accomplishing this is shown in Figures D7a and D7b.

A cassette for dispensing a layer of dispersion at the top of the cell is built into the cell cap. The cassette consists of a mesh, for holding the dispersion, which is sandwiched between a plunger and a support screen. The surface tension of the dispersion and the mesh/screen retain a thin layer of dispersion after it is extracted by a spring loaded plunger. This cassette is loaded by a process shown in Figure D7a. With plunger compressed, the cassette is inserted into the loading cell which is then filled with the particle dispersion. The plunger is then released slowly to allow a spring to withdraw the plunger and a thin layer of dispersion into the cassette to the retracted position. The spring could be replaced by threads on the cap which would allow the cap to be threaded in and out to extract or inject sample. Now when the loaded cassette is turned upright, the dispersion layer is held in the cassette by surface tension of the liquid and the mesh/grid structure, as shown in Figure D7b. The loaded cassette with retracted plunger is inserted into a centrifuge (or settling) cell, which is filled with clean dispersant. The cassette seal fits the cell opening, allowing air bubbles to pass around the seal as the cassette is inserted. This creates a sealed cell, without air bubbles, filled with clean dispersant. The plunger is then slowly compressed (or threaded in) to push the particle dispersion layer into the top of the clean dispersant. This layer is so small, that the additional volume of the layer is accommodated by slight distortion of the cassette seal or slight leakage past the seal. The plunger is then locked into the compressed position with a clip or other means. The loaded cell is placed into a centrifuge for centrifugation or simply set vertically to allow gravitational settling of larger or denser particles. The

user could also wait until after the cell is placed into the centrifuge or settling stand, to compress the plunger, to avoid any distortion of the particle layer due to cell movement while being placed into the centrifuge or settling stand. After centrifugation or settling, the cell is scanned by either a static or dynamic scattering system to determine the size distribution as described previously. During transfer to the scattering instrument, agitation of the cell must be avoided to prevent movement of the particles from their separated bands. But if some mixing does occur, the scanning analysis will detect it and correct the size distribution, because the entire particle size distribution is measured over each R region.

This process could also be accomplished with a cell cap which has only the mesh and/or screen, without the plunger and spring. If the thin mesh and/or screen is immersed into the particle dispersion and agitated, the dispersion will fill the mesh and/or screen and be held by surface tension for transfer to the cell. Then when the cap is placed onto a cell with clean dispersant, the clean dispersant will wet the air/particle dispersion interface of the cap, reducing the surface tension forces. During the centrifugation process, the particles will be pulled out of the mesh and/or screen into the clear dispersant by the centrifugal force.

In both the layer and homogeneous start cases, the duration and centrifugal acceleration (determined from centrifuge rotation speed) of the centrifugation must be controlled so that the particle sizes of interest remain in suspension and that sufficient separation of the sizes occurs. If the duration is too short, you will have poor separation. If the duration is too long, some of the larger particles may all be impacted on the bottom surface of cell (or the large R end of the cell), where they cannot be detected by the scattering system. The duration could be optimized by scanning the cell after a short duration to determine the distance which the largest particles have moved. Then the computer could calculate the additional duration and rotation speed required to spread the particles, in the size region of interest, across the cell for maximum separation and size resolution.

Another advantage of this method is the reduced sensitivity to particle composition. In other ensemble particle size methods, such as dynamic and static light scattering, the major need for an accurate scattering model (particle and dispersant refractive indices, and particle sphericity) is to account for light scattering from particles of one size interfering with light scattered by particles of another size. This usually causes the incorrect presence or absence of addition modes or tails in the particle size distribution. However, since the particles are spatially separated by size before scanning, there is very little scattering crosstalk between different sizes. This is true for both the layer and homogeneous start cases because both of them separate the scattered signals to be representative of certain size bands. The layer start case does it directly and the homogeneous start case uses subtraction of a prior signal to create a differential signal input from a cumulative spatial distribution. In fact, if the spatial separation is clean, the scattering model can be determined from the scattering data sets collected over the cell scan by either using equation 1 or equation 1a to determine the hydrodynamic size, or by using the maximum calculated optical size (from scattered light measurements) for that region.

For very broad particle size distributions, the largest particles may reach the end of the centrifuge cell before the smallest particles have moved a sufficient distance to provide good size separation. In this case the total size distribution may be created from a group of scans of the centrifuge cell at various centrifugation periods. To accomplish this, the first scan will determine the largest particle size in the sample. Then the computer will determine the added centrifugation period required to drive the largest particles to the end of the cell. After this period, the cell is scanned again to produce the first particle size distribution. The next centrifugation period is calculated to drive the smallest well detected size, of this latest scan, to the end of the cell. This sequence of scanning the cell, size measurement, and calculating the period for the next centrifugation cycle is repeated until the smallest particles have moved sufficiently to be clearly resolved in size. Since the sample cell must be removed from the centrifuge and placed into the scanning scattering system during each

cycle, this process can be labor intensive. Figure D8 shows a method for automating this process. The centrifuge rotor and motor are mounted to a scanning stage which allows the optical system to scan the cell during centrifugation. Then the process described above could be accomplished completely under computer control without intervention. The light source is pulsed to illuminate the sample when it is aligned with the light beam during each rotation of the centrifuge. The angular distribution of scattered light at each position along the X direction is constructed from integration of the scattered light from many source pulses at each X position. The system in figure D8 is somewhat complicated to manufacture. Another possibility is to place sources and detectors in a conventional centrifuge to determine when the particles have reached the end of the sample cell or when the particles have left inner radius of the cell. A scatter detection system (detector, source, and optics) is placed on each end of the sample cell to detect when the particle concentration increases above some limit at the far end (large X or R) and when the particle concentration drops below some limit at the near end (small X or R). When either of these events occur, an audible alarm or light indicator is set to tell the operator to turn off the centrifuge and remove the cell for scanning by a scatter instrument. The detectors and sources, which travel with the rotating centrifuge, are powered by batteries in the centrifuge rotor. The particle concentration vs. R distribution or particle size distribution determined from this first measurement can determine the centrifuge settings (rotation rate and period) for any additional centrifugations or settlings. The repeated sequence of scanning the cell, size measurement, and calculating the period for the next centrifugation cycle can also be accomplished with the systems shown in Figures D23 and D24, which are described later.

Once the effective particle density viscosity ratio or K value is determined from the first particle size scan or from the known value for the material, the hydrodynamic diameter which corresponds to each value of X could be determined from Stokes equations (equation 1a or 1). Then the particle size distribution could be determined by measuring the particle concentration vs. X. The particle concentration can be determined from the scattering extinction or total scattered

light at each X position over a limited size range. This process will produce a particle size distribution based upon hydrodynamic diameter of the particles, while the scattering techniques, described above, produce an optical size. Below approximately 5 micron particle diameter, the scattering crosssection becomes particle size dependent and the particle volume must be corrected for changing scattering crosssection.

In the cases shown above, the direction of centrifugal force should be parallel to the gravitational force to avoid settling of the particles on to the cell window. However this is usually not required in the centrifuge because the centrifugal acceleration is usually over 1000 times the gravitational acceleration and the length to thickness ratio of the cell might be only 20:1. In this case, only a small fraction of the largest particles will settle and contact the window. But if this settled fraction becomes significant, then the direction of centrifugal force should be made parallel to the plane of the gravitational force vector to eliminate this problem.

In the case of particle separation by gravitational settling, the cell could be scanned by the scattering system during the settling process. If the sample were settled outside of the scattering instrument, mixing of the separated particles could occur during insertion of the cell into the scattering instrument. By starting the particle settling in the scattering instrument, the cell never has to be moved during the entire process and the cell scan can be performed at various times during the settling process to improve size resolution.

The angular scattering measurements may contain speckle noise if a laser source is used. The speckle noise will cause errors in the scattered light measured by each detector. If the particles move a small amount during the signal collection, the speckle noise will average out and the errors will be reduced. This averaging process can also be accomplished by averaging the scattered signals from groups of angular scattering signal captures which are individually taken from slightly different X positions. In other words, each scattering data set, used in the analysis, is the average of many angular signal set captures, each one from a slightly different X (or R) value. The distance



of each step (perhaps a few microns) between each of these signal captures is much less than the step (greater than 50 microns) between each analyzed data set. So the X (or R) value for each data set would be the average X (or R) value over the group of captures for that data set. This process will reduce the amount of speckle noise in the scattering pattern and improve the accuracy of the measured scattering signals. An ultrasonic probe could also be placed into the dispersion during data collection to induce small amounts of particle motion during a single data collection (signal integration) period to average out the speckle, however this may distort the layered structure of the particle dispersion.

The homogeneous particle sample could also be placed into the scattering instrument before centrifugation to determine the approximate particle size distribution by angular scattering from the particle ensemble. With knowledge of the dispersant viscosity and density, and the particle density, the proper centrifuge settings of centrifugal acceleration (rotation speed) and centrifugation duration are calculated by a computer algorithm using equation 1 above to insure that the largest particles just reach the large R value end of the sample cell by the end of the centrifugation. In this way the maximum size separation and particle size distribution accuracy is obtained. If the user requests analysis of a certain size range, the computer can use equation 1 to determine the centrifuge settings which will spread the particles in that range across the full length of the cell. Of course, a reasonable estimate of the particle density is needed to compute these settings. This pre-centrifugation/settling measurement of a homogeneous sample could be used to calculate the above parameters for both the homogeneous and layer start cases.

For large dense particles, the settling or centrifugal induced terminal velocities may be too large to obtain a controlled spread across the sample cell. Also, particles may settle to the bottom of the cell while the cell is being inserted into the scattering instrument. In this case, dispersants with higher viscosity could be used to allow spatial/size separation of large dense particles in the centrifuge. Then after centrifugation, the particles are held in place by the high

viscosity. For example, glycerin could be added to water dispersant to adjust the viscosity to reduce the terminal velocities of the largest particles so that centrifugation can easily distribute the particles across the cell and that distribution is held in place during transfer of the cell to the scattering instrument.

The scattering efficiency problems described at the beginning of this disclosure are worst for particles of diameter below approximately 5 microns. Therefore, these techniques are usually applied below a few microns where the scattering angles are larger and angular alignment tolerances are relaxed. Under these relaxed alignment conditions, the sample cell, filled with clear dispersant, could be inserted into a holder, in the instrument, which registers the cell into a corner under spring load. The source beam is then aligned to the appropriate point on the detector array. The cell is then scanned to obtain the scattering background at various R values along the cell. A known small amount of concentrated particle dispersion is injected into the cell. This cell is agitated to provide a homogenous concentration and then the cell inserted back into the holder. The instrument collects one set of scattering data. Based upon the scattered signal intensities, the instrument calculates the amount of additional concentrated particle dispersion which should be added to the cell to provide optimal scattering signal levels, as illustrated in figure D9. The instrument also estimates the particle size distribution to determine the optimal settings for the centrifuge, using the particle density, and the density and viscosity of the dispersant, with equation 1 or 1a. The cell is removed from the instrument and centrifuged. After centrifugation, the cell is inserted back into the position registration holder in the instrument and the cell is scanned by measuring scattering data at various R values as described above. This pre-centrifugation/settling measurement of a homogeneous sample could be used to calculate the above parameters for both the homogeneous and layer start cases.

Figure D3B shows a method for scanning the centrifuge cell with an external dynamic light scattering system. This procedure requires that the centrifuge cell be removed from the

centrifuge, unless the optical system is built into the centrifuge system. Both of these modes are claimed by this disclosure. However, use of a commercial centrifuge and an attached optical system may be more practical. This also avoids any potential distortion of the spatial particle distribution inside of the cell as it is moved from the centrifuge to an external optical system and this concept provides for automated multiple scans at various times during the centrifugation process, by stopping the centrifuge, scanning, and restarting the centrifuge, under computer control, as described previously. A stationary optical system could be mounted on top of a commercial centrifuge to scan the centrifuge cell in the centrifuge after spinning has stopped. Many systems could be designed to fit into the centrifuge, using the ideas already proposed in this disclosure, using either angular scattering (static scattering Figure D3) or dynamic scattering. However, another approach is to scan the dispersion in the cell with a small probe, which can be moved throughout the cell with a computer controlled actuator, as shown in Figure D23. This configuration uses a fiber optic dynamic light scattering system as described previously. The fiber optic port in the dispersion can be simply the bare fiber end, which will produce sufficient reflection for heterodyne mode and could also work in homodyne mode by eliminating that reflection. The fiber optic, which may be less than 200 microns in diameter, could be supported inside of stainless steel tubing such as that used for hypodermic needles. Hence a needle like probe could be inserted into the dispersion. Scattering signals would be collected at various locations along the direction of the centrifugal force in the cell to measure particles which have been separated in size by the centrifugal force or gravity, as described previously. However, in this case the scan is completed while the cell is still in the centrifuge. The scanning motion actuator and fiber system are mounted above the centrifuge. The cell is centrifuged without a cell cap so that the actuator can insert the fiber into the top of the cell, after the centrifuge has stopped and moved to the nominal position for insertion, as shown in Figure D23. The optical system is then moved by the actuator to move the probe to various positions in the cell and digitize the detector signal for a sufficiently long time to accurately produce the power spectrum or autocorrelation function of the

detector signal at each location. Then these data sets are used to determine the particle size distribution as described in the previous disclosure by this inventor. The entire process of completing these multiple measurements is called a scan. Since the fiber optic probe is so small, it does not effect the spatial particle concentration distribution in the cell, because it displaces a minimal volume of dispersion as it moves through the cell. And data is collected from the cell opening to the cell bottom to measure undisturbed dispersion at each step. The probe would also be stepped sideways between each scan so that it would avoid scanning through dispersion which had been disturbed by a previous scan. Therefore, the cell could be scanned at multiple times during the total sample centrifugation to measure different particle size ranges, all under computer control without user intervention. By sensing the particle concentration and size at shortest and longest centrifuge radius, the computer could determine when the centrifugation should stop. Using particle density and size, the computer could calculate the time required to separate the next particle size group from the shortest radius region. When this time becomes too long, the centrifuge could warn the operator and/or stop. When particles at the smallest size end of the range of interest are absent from the region of shortest centrifuge radius in the cell, the centrifugation can be stopped. It could also be stopped when only the smallest particles of interest remain at the shortest centrifuge radius.

The tip of the fiber in the dispersion could be bent at various angles to provide the least disturbance to the dispersion or it could be bent at right angle to avoid Doppler shifts from settling particles by bending the tip so that the optical axis of the fiber is perpendicular to the settling direction. But normally settling will not be a problem, if centrifugation is required to obtain particle motion. Most angles will work well, but a straight fiber probe would provide the least disturbance to the dispersion so that multiple scans can be made in different portions of the cell without affecting each other.

The disturbance to the particle concentration distribution can be avoided completely by using a scanning system which does not contact the dispersion as shown before in Figure D3. The sample

cell would be scanned by moving the optical system, shown in Figure D3, along the sample cell, while the sample cell resides in the stopped centrifuge, after centrifugation is complete. Another concept, which could replace that design, is shown in Figure D24. This system measures dynamic light scattering signals at two scattering angles, 180 degree scatter back through fiber optic coupler A (detector A) and lower angle scatter through fiber optic coupler B (detector B), which operate in heterodyne or homodyne mode through selection of the fiber optic switch between port 3A and 3B. This system has the flexibility of operating at multiple scattering angles and switching to homodyne mode, when excess laser noise causes high error in the heterodyne mode. As before, the interaction volume of the optical system, which is the intersection between the light beam from port 4A and the field of view of port 4B, is scanned along the direction of the centrifugal force in the cell. The optical system projects light and receives scattered light through windows in the sides of the cell. Fiber optic coupler A directs light into the cell and collects scattered light back through port 4A. Fiber optic coupler B receives scattered light through port 4B. This scattered light can be detected directly in homodyne mode by opening the fiber optic switch between ports 3A and 3B; or it can mix the scattered light with source light by closing the fiber optic switch, to operate in heterodyne mode. In homodyne mode, detector B may need to be a photon multiplier or avalanche photodiode for sufficient sensitivity. Photon counting may also be employed to provide sufficient sensitivity for the very small homodyne signals. This design is also claimed for application in conventional dynamic light scattering applications where centrifugation is not used.

Some advantages of these methods are listed below:

- 1) Samples with very low density differences between the dispersant and the particle are difficult to measure due to the high sensitivity of size to small errors in density. The methods described above can provide accurate size measurements even for samples with low density differences between the dispersant and

the particle, because the size can be measured from optical scattering.

2) When the density difference between the dispersant and the particle is small, particle diffusion can become significant as compared to the terminal velocity. The methods described above will provide accurate size distribution for these cases.

3) The size accuracy is not sensitive to particle composition because the effects of large angle scattering tails, from larger particles, on the scattering of smaller particles is reduced by the spatial separation of particles based upon size.

4) The best information can be used to determine the particle size distribution. If the spatial distribution of the particles provides better particle size accuracy (using scattering measurements to determine the particle concentration distribution vs.  $R$  and equations 1 or 1a to determine the hydrodynamic size at each value of  $R$ ), then it will be used instead of the size distribution calculated from the static or dynamic scattering distribution alone.

5) The scattering efficiency function could be produced empirically from the spatially separated modes of samples with known mixture ratios because each mode is measured individually in the same sample. There would be no need for absolute scattering measurements of individual samples.

6) Knowledge of the dispersant viscosity and density, and particle density, are not required to obtain accurate particle size distribution measurement when using the scattering distribution to determine size at each value of  $R$ .

#### **Real time measurement of terminal velocity**

High resolution particle size measurement has not been demonstrated for particle ensembles. High size resolution can only be obtained through sample dilution and individual particle counting. However, the count accuracy of particle counters is

limited by Poisson statistics of the counting process. This is particularly problematic for broad distributions commonly seen in industrial processes. The following describes a methodology for measuring particle size distributions of particle ensembles, with high size resolution and volumetric accuracy. This is accomplished by measuring the terminal velocities of particles in a centrifugal force field, produced in a rotating centrifuge.

Figure D10 shows the concept of this invention. The particle dispersion is injected into a sample container or cell, which has two optical windows. Two beams of light, originating from the same light source, intersect within the dispersion between the windows. An optical source, such as a laser diode, is nearly collimated by lens 1. This beam is split by a beam splitter to produce two mutually coherent beams of light, the first of which passes through the particle dispersion and is focused by lens 2 through a pinhole onto an optical detector. The second beam is reflected by a mirror to intersect the said first beam within the particle dispersion. The scattered light from said second beam is also focused through the same pinhole to produce a heterodyne optical signal on the detector, whose frequency is indicative of the velocity of the particles. In this heterodyne configuration, said first beam is the local oscillator and the angle between said first and second beams defines the measured scattering angle for light scattered from said second beam by the particles. This angle could be sufficiently small to avoid MIE scattering efficiency resonances and Brownian motion spectral broadening; but the angle must be sufficiently large to produce large Doppler shifts. For particles below approximately 200 nanometers diameter, the Brownian spectral broadening may be used to determine size. The detector signal is amplified and high pass filtered to separate the beat frequency portion of the heterodyne signal from the large unwanted zero frequency component.

The entire sample, container, and optical system are contained in an arm of a rotating centrifuge. Near to the center of rotation is a battery and electronics for powering the detector and light sources. The high pass filtered signal is transferred from the rotating system to the A/D converter of a stationary computer through an optical rotary connection consisting of an

optical source, such as an LED, which rotates with the centrifuge and a stationary optical detector. The LED intensity is modulated by the high pass filtered signal and read by the stationary detector to transfer the signal to the A/D. This rotary connection could also be accomplished by radio transmitters, digital storage devices and electronic rotary connectors, some of which use mercury for conduction of the signal. The use of the high pass filter is critical to maintain signal integrity through this rotary connection. The enormous zero frequency component of the heterodyne signal could produce spurious signals in the rotary connection, in the spectral region of interest.

If the A/D converter were placed in the rotating electronics, then digital light (or electrical) signals could be transmitted through the rotary connection (or by other means mentioned previously). This system would be relatively immune to noise in this connection and would provide easy access to scattering signals from multiple detectors by time multiplexing. The advantages of measuring scattering signals at various scattering angles are discussed later in this disclosure.

The velocity of the particles being pulled by the centrifugal force depends upon particle size and density. Larger or denser particles will attain larger velocities and produce higher heterodyne beat frequencies. The local velocity over a small region about centrifugal radius R is given by  $V_0$  below:

$$(1) \ln(R_2/R_1) = 2(w^2)(p_1-p_2)(D^2)t/(9q) \quad (\text{from previous description})$$

$$V_0 = k_1 \cdot R$$

$$\text{Where } k_1 = 2(w^2)(p_1-p_2)(D^2)/(9q)$$

Any particle of a certain size and density will produce a narrow heterodyne spectrum, which can easily be separated from the narrow spectra of other particles of nearly the same size and density, resulting in high size (and density) resolution and accuracy. The spectrum of a particle ensemble, with a multimodal size distribution, will consist of a group of line spectra which only need correction for scattering efficiency to produce



accurate particle size distribution. Other spectral broadening mechanisms must also be considered.

The distance (or scattering pathlength) between the windows may be shortened to lower multiple scattering when measuring high concentration particle dispersions. Also the optical system could be folded to create a compact system which could be inserted into a commercial laboratory centrifuge. Also the beamsplitter could be replaced by a fiber optic coupler. Other configurations of heterodyne systems for measuring particle velocity are also possible and are claimed for use in this invention.

Usually centrifuges have long speed ramp up and slow down periods. Also different centrifuge speeds may be used to cover different particle size ranges. Therefore, the heterodyne spectrum should be corrected for the actual centrifugal force by monitoring the rotational velocity of the centrifuge and shifting the relationship between size and heterodyne spectral frequency accordingly.

Another aspect of this invention is the method of introducing the particle dispersion into the sample container. For low concentration samples, a scattering background signal should be measured with clear dispersant and then the particle dispersion should be measured separately; and these two spectra are then subtracted from each other to eliminate the effect of system background scatter and noise. This is easily accomplished by employing a compression seal at the inlet and a low pressure relief valve at the outlet of the container. The compression seal could match the tapered end of a syringe body and plunger (without syringe needle) so the sample or dispersant could be forced into the container under pressure, forcing the prior sample out through the relief valve. Then a user could repeatedly introduce various particle samples (or dispersants for background) without turning any valves between each sample change. The syringe body tip is pressed into the inlet seal and the plunger is then used to force the prior sample out through the relief valve. The contents of the sample container can also be blown out by using an empty syringe (or compressed gas) to

force air or gas through the container. A bypass valve is also used for flushing the sample container.

Larger or denser particles will have high velocities, due to the centrifugal force, and these particles will all move through the sensing region too quickly to obtain a spectrum. In these cases, the sample cell and optical system can be oriented to allow gravity to provide a much lower force on the particles, with the gravitational force nearly along the same direction as the centrifugal force, as indicated in Figure D10. By using gravity as the lowest force and varying the centrifuge rotational speed, a large range of particle size and density can be accommodated, by varying the force on the particle ensemble.

The sample could also be placed between two flat transparent windows, which could be disc shaped. The outer edges of these discs are sealed to provide a thin disc shaped sample cell. The particle dispersion is then injected to fill the cavity between the disc windows. The disc sample cell is spun about its axis of symmetry perpendicular to the disc plane. The particles will accelerate along the tangential direction of rotation and reach nearly the same rotational speed of the discs. The centrifugal force will pull the particles out radially. An optical system, as shown in Figure D10 would view through the rotating disc to measure the radial particle velocities and particle size distribution. In this case the optical system, consisting of the light source, lens 1, beamsplitter, mirror, lens 2, pinhole, detector, and all electronics would be stationary. Only the disc sample cell and particle dispersion would rotate. Most of Figure D10 would still apply except that the particle sample container crosssection would be the crosssection of the disc sample cell, without need for a rotating signal coupling because the optical system would not be part of the rotating assembly.

Theoretically, the tangential velocity component of the particles would be perpendicular to the scattering plane and hence it would produce zero Doppler frequency shift in the scattered light spectrum. However, a beam of finite size would view some particles with velocities which are not perpendicular to the scattering plane and would produce a scattering spectrum

which interfered with that due to the radial centrifugal component. Therefore the scattering plane could be adjusted to not be parallel to the radial direction. The angle between the scattering plane and radial direction would be adjusted so that the narrow Doppler shifted spectrum, due to the tangential velocity component, would be shifted to frequencies well above that of the radial velocity distribution to avoid interference between the two spectra. The anti-aliasing filter must remove frequencies from this tangential velocity spectrum, which alias into the spectrum from the radial velocity component. Likewise, the tangential velocity of dust and other scatterers on the disc surfaces will also produce spectra, which are shifted to higher frequencies and further removed by background subtraction (by measuring the spectra without particles present in the cell).

Another advantage of these ideas is the ability to electronically change the particle size range and size resolution by adjusting the ADC sampling rate and anti-aliasing filter. Once the particles reach terminal radial velocity due to the centrifugal force, a broadband spectra could be measured to determine the frequency region of the Doppler spectrum. Then the sampling rate would be adjusted to optimize resolution in that frequency region. The user could also adjust the sampling rate to look at fine details of the particle size distribution in certain size ranges. After entering a size range of interest, the computer would calculate the proper sampling rate and anti-aliasing filter parameters to optimize size resolution.

The power spectrum of the optical detector current contains a constant local oscillator and a frequency dependent component. The frequency dependent component is described by the following equations:

$$P(f) = (S(d,a,nm,np)^2) * (E * G^2) / (4\pi^2 * (f - G * v)^2 + (EG^2)^2)$$

where  $G = 2 * nm * \sin(a/2) / w_l$

$$E = kT / (3 * \pi * \eta * d)$$

$$v = c * (pp - pm) * (d^2) * a$$

$P$  = power spectrum of the detector current  
 $S$  = scattering efficiency per unit particle volume  
 $d$  = particle diameter  
 $\rho_p$  = particle density  
 $\rho_m$  = dispersant density  
 $\eta$  = dispersant viscosity  
 $f$  = frequency  
 $n_p$  = refractive index of particle  
 $n_m$  = refractive index of dispersant  
 $\alpha$  = scattering angle  
 $v$  = terminal particle velocity  
 $c$  = constant which depends on dispersant viscosity and particle shape  
 for spherical particles  $c = 2/(9\eta)$   
 $^2$  = square of quantity  
 $g$  = acceleration due to centrifugation or gravitational settling  
 $k$  = Boltzmann's constant  
 $T$  = dispersant temperature  
 $\lambda$  = wavelength of the source light

This equation can be reduced to the form:

$$P(f) = c \left( \frac{\sin(\alpha/2)}{\lambda} \right)^2 \frac{S(d, \alpha, n_m, n_p)^2}{(f - f_s)^2 + f_b^2}$$

where

$$f_s = B d^2 \sin(\alpha/2) g (\rho_p - \rho_m) / \lambda \quad \text{Doppler frequency shift due to terminal velocity}$$

$$B = 2n_m c$$

$$f_b = c \left( \frac{\sin(\alpha/2)}{\lambda} \right)^2 / d \quad \text{spectral broadening due to Brownian motion}$$

The light scattering intensity  $S(d, \alpha, n_m, n_p)$  per unit particle volume and per unit incident light irradiance depends upon the scattering angle ( $\alpha$ ), particle diameter ( $d$ ) and refractive indices of the particle ( $n_p$ ) and dispersant ( $n_m$ ). This scattering efficiency is small for small particles and grows with increasing particle diameter up until approximately 1 micron. Above 1 micron, the scattering efficiency oscillates

versus particle diameter. This behavior depends upon the scattering angle and refractive indices, but the behavior is similar for most types of spherical particles. The oscillations are caused by optical interference between the light diffracted by the particle and transmitted by the particle. For non-spherical particles these oscillations are dampened by the random orientation of the scatters. So in general, the amplitude of these oscillations may be difficult to predict. The best strategy is to choose optimal scattering angles where oscillations are small but will still give sufficient Doppler shift to avoid low frequency noise in the detector electronics, through filtering.

The larger scattering angles provide larger Doppler frequency shifts for a given particle velocity. Hence, larger scattering angles are needed for smaller particles which have lower velocities in the centrifugal force field. Also, small particles produce less scattered light per unit particle volume. Therefore the optical detector must subtend a larger angular width to generate sufficient signal level. The Doppler shift is proportional to the sine of half of the scattering angle. The angular subtense of the detector must be small for two reasons: to include only a few coherence areas on the detector and to reduce the spectral spread due to the variation of Doppler frequency with scattering angle.

As shown above, the Doppler shift is proportional to  $\sin(a/2)$ . For small, low density particles such as 0.1 micron polystyrene spheres, centrifugal accelerations of 100,000 G's will produce 10 Hertz Doppler frequency at 10 degrees scattering angle. And this frequency increases proportional to the square of the particle diameter. At a 10 degree scattering angle, the scattering efficiency is a well behaved function of particle diameter below 1 micron particle diameter. Above 1 micron, the 10 degree scattering efficiency shows many large oscillations as a function of particle diameter, while the scattering efficiency at 1 degree is smooth and well behaved. The Doppler shift for 0.1 and 1 micron particles are 1 Hertz and 100 Hertz, respectively at 1 degree, and 10 and 1000 Hertz, respectively at 10 degrees. Therefore, to cover an extended size range, the scattered light must be measured at multiple angles to provide

sufficient Doppler shift for small particles (using large angles) and to avoid scattering resonances for larger particles (using small angles). Larger angles are also needed at lower acceleration levels, to maintain sufficient Doppler shifts. By measuring multiple scattering angles, the size regions where scattering efficiency oscillations occur may be avoided by solving the problem in regions of well behaved scattering efficiency.

This invention will greatly improve both the accuracy and resolution of particle size measurement over a large particle size range, because each particle will create a narrow detector current power spectral line whose position is size dependent. The spectrum consists of a symmetrical Lorentzian Brownian broadened spectrum which is shifted by the Doppler frequency of the terminal velocity. As the scattering angle decreases, the Brownian spectral width decreases relative to the Doppler shift and the size resolution increases. Smaller particles have a broader Brownian spectrum and smaller Doppler shift. The scattering angle should be large enough to push the Doppler spectrum above the low frequency noise of the system, but very large angles will degrade size resolution, because the Brownian spectral width will become comparable to the Doppler shift. In general this tradeoff cannot reduce the spectral line broadening to negligible levels. And so this broadening must be accounted for in the theoretical model. This Brownian broadening could be reduced by using the same deconvolution techniques as described previously for measurements of Zeta potential. However the effects of broadening can also be resolved by measuring the power spectra (or autocorrelation functions) of the optical scattering light detector at various scattering angles and various accelerations. The particle volume distribution (the particle volume per unit particle diameter interval) can be determined from these multiple spectra, by solving a single set of linear equations as shown in the matrix equation shown in Table 1.

**Table 1**

P(f1,a1,g1)	P(f1,a1,g1,d1)	...	P(f1,a1,g1,dn)	
P(f2,a1,g1)	P(f2,a1,g1,d1)	...	P(f2,a1,g1,dn)	
.	.		.	V(d1)
.	.		.	V(d2)
P(fm,a1,g1)	P(fm,a1,g1,d1)	...	P(fm,a1,g1,dn)	.
.....	.....		.....	.
P(f1,a2,g1)	P(f1,a2,g1,d1)	...	P(f1,a2,g1,dn)	.
P(f2,a2,g1)	P(f2,a2,g1,d1)	...	P(f2,a2,g1,dn)	.
.	=	.	.	.
.	.		.	.
P(fn,a2,g1)	P(fn,a2,g1,d1)	...	P(fn,a2,g1,dn)	.
.....	.....		.....	.
P(f1,a2,g2)	P(f1,a2,g2,d1)	...	P(f1,a2,g2,dn)	V(dn)
P(f2,a2,g2)	P(f2,a2,g2,d1)	...	P(f2,a2,g2,dn)	
.	.		.	
.	.		.	
P(fn,a2,g2)	P(fn,a2,g2,d1)	...	P(fn,a2,g2,d1)	

V(d) is the volume distribution versus the particle diameter (d). Each power spectrum is the addition of all the power spectra from each particle in the scattering volume, which is the intersection of the particle sample and the incident light beam. Table 1 shows one example, where the power spectral density is measured at various frequencies (f1,f2,...fn), scattering angles (a1,a2) and acceleration levels (g1,g2). These spectra create a set of linear equations, which are usually overdetermined and solved by least square or other iterative techniques to obtain the volume distribution V(d). The most straight forward method is to simply invert the matrix equation in Table 1. The equation for P(f) given above is used to calculate the elements of the matrix in Table 1. All of the examples given so far are only for illustration, this invention assumes that any number of accelerations, scattering angles, and detection frequencies may be needed to optimize the condition of this system of equations. Also power spectra may be replaced by their inverse Fourier Transform (the autocorrelation function of the scattered detector) to form a similar set of equations in

time instead of frequency space. However, the best performance will be seen by using the power spectrum, because the spectrum of each particle is clearly separated in frequency space.

Also these different spectra may be solved as separate linear systems if this is advantageous. Notice that the Doppler frequency shift ( $f_s$ ) is proportional to the difference ( $\rho_p - \rho_m$ ) between the particle and dispersant densities and the acceleration ( $g$ ). However the Brownian width does not depend on the density difference. Therefore, this density difference can be determined by solving for the density difference as a parameter in the equation set, by using non-linear techniques.

Techniques for reducing the effects of spectral broadening due to Brownian motion are the same for Zeta potential and centrifugal systems. In both cases, the particle velocity distribution due to the preferred force (electric field for Zeta potential and centrifugal or gravitational force for particle size) is broadened by Brownian motion. Therefore any broadening reduction method, used in one measurement type, can also be used in the other. For example, the matrix equation in Table 1 could be used with Zeta potential by replacing the theoretical model for centrifugation with the model for electric mobility. Then the accelerations ( $g_1$ ,  $g_2$ , etc.) would be replaced by various electric field levels and the form of equations in Table 1 could be used to improve resolution in Zeta potential measurements.

The following describes various optical configurations for measuring the spectral characteristics of scattered light at multiple angles.

All optical configurations in this disclosure assume the following:

The designs can be extended to any number of scattering angles. The sample cell or sample container may refer to either the disc shaped cell (which rotates without optics or electronics) or the small cell (which rotates with the optics and electronics).



### Fiber optic configuration 1

This configuration uses fiber optics to carry light to and from the particle sample (see figure D11). The fibers also collect light from separate scattering angles and mixes that light with light from the source, using fiber optic couplers. The light source, which may be a laser, is focused, by lens 1, into the source fiber optic. The beam exiting this fiber is nearly collimated by lens 2 to produce the incident beam (red rays) for the particles. Lens 3 focuses the scattered light into multiple fibers. Each fiber intercepts a different range of scattering angles as indicated by the blue and green rays. The incident beam (red rays) is also collected by a fiber optic to provide the local oscillator which is mixed with these separate scattering beams by using fiber optic couplers. Fiber optic coupler 1 splits the source light into two or more fibers to be further mixed with scattered light in the other fiber optics, using couplers 1 and 2. The power spectrum of detector current for the low and high detector will follow the theory described above. The amount of light transmitted by the sample may also be measured to help in optimizing particle concentration to avoid multiple scattering.

### Fiber optic configuration 2

The second fiber optic configuration is similar to the first, except that the source light is split off from the source fiber, by fiber coupler 4, and mixed directly with the scattered light using fiber optic couplers 1 and 2, as shown in figure D12.

### Beamsplitter configuration 1

This configuration uses beamsplitters to provide the local oscillator (see figure D13). Again the source beam is nearly collimated by lens 1 and folded through the sample cell by mirror 1. Mirror 2 folds the incident beam and scattered beams through lens 2, which focuses these beams onto an array of mask apertured detectors. The beam color coding is equivalent to the fiber case. A small portion of the source beam is split off by

beamsplitter 1 to provide the local oscillator to be mixed with the scattered light on the detector. An optional grating or optical wedge (only partially placed in the beam) could provide multiple local oscillator beams which would line up with each of the scattering detector apertures. And lens 3 may be used to defocus the local oscillator beams to lower alignment problems at the mask. Beamsplitter 2 folds these local oscillator beams through lens 2 to be mixed with scattered light on each detector.

#### Beamsplitter configuration 2

In this configuration, the local oscillator is provided through the scattering volume, as shown in figure D14. Notice that the 3 beams passing through the sample cell are numbered 1, 2, and 3. Beam 1 is the incident beam, which creates the scattered light. Beams 2 and 3 are local oscillator beams which mix with the scattered light at various angles. Again these mixed beams are focused by lens 2 onto an array of mask apertured detectors. Beamsplitter 1 and 2 provide the local oscillators at the various scattering angles. The reflectivity of these beamsplitters should be optimized to produce the largest heterodyning signal on the detectors.

The Doppler frequency shift changes with scattering angle. Therefore, collection of scattering over wide range of scattering angles will create significant broadening of the shifted spectrum, requiring deconvolution to retrieve size resolution. However, collection over a narrow angular range will maximize the errors caused by Mie resonances. By measuring over a wide range of scattering angles, the Mie resonances are washed out. This is accomplished by measuring the scattered light from particles flowing through a modulated light pattern, such as a group of interference fringes. As the particles flow through the fringe pattern, the scattered light from each particle is modulated with a frequency indicative of particle velocity and size. The spectral width of the scattered light is not broadened significantly by collecting scattered light over a wide range of angles in this fringe field, which may be produced through interference between two light beams as shown in Figure D15.

A coherent light source, such as a laser diode, is focused or collimated into the sample container by lens 1. A beamsplitter produces a second beam 2 which creates interference fringes with beam 1 in the sample container. Light scattered by particles in the fringe region is collected by lens 2, which focuses this light onto a detector. The signal from the detector may (or may not) be electronically filtered before being transmitted to the stationary A/D. In this case, a radio transmitter is used in the rotating system to transmit the scattering signal to a stationary radio receiver at the input to the A/D. Commercially available wireless FM, Blue Tooth, or wireless digital microphone technology could be used to transmit the digital or analog data from the rotating centrifuge to the stationary computer. These devices have sufficient signal to noise and bandwidth. The detector signal could also be stored in digital storage (memory chip) in the rotating system and then read out by connection to the computer after the centrifuge has stopped. The optical rotational coupling, radio transmitter, and digital storage are three means of transferring the scattered light signal from the rotating system to the stationary computer. All three of these techniques are claimed for all configurations associated with this disclosure.

Figure D16 shows another variation of this fringe system, with more detail of the collection optics. Usually the fringe field will be imaged onto the detector to provide discrimination against other light sources. And the angular acceptance may be large with minimal effect on the scattered signal spectrum, because the fringe field modulates the scattering amplitudes at all scattering angles.

Since the target image has limited depth of focus in the sample container, some particles will pass through regions where the fringes are out of focus. This will cause broadening of the modulation spectrum and the impulse response of the linear system which describes the scattered signals. By reducing the pathlength through the sample container, the particles may be restricted to the region of best focus for the target. Alternatively, the resulting scattering signal spectrum may be deconvolved by including the spectral broadening in the

scattering model and inverting that model by use of iterative optimization techniques or deconvolution.

Even with wide angular collection, Mie resonances may still be a problem for narrow wavelength bandwidth sources. Another problem is size dynamic range. A single fringe spatial frequency can only handle particles with diameters smaller than the inter-fringe spacing, but with sufficient size (and velocity) to cause high modulation frequency. A particle, which is much smaller than the fringe inter-fringe spacing, may travel too slowly to produce a scatter signal modulation frequency above the  $1/f$  noise of the detection system. Fringe patterns with smaller inter-fringe spacing are needed for small, low velocity particles. The best solution is multiple fringe spacings. By using multiple beamsplitters and detectors, multiple fringe fields may be created with different inter-fringe spacings. Each fringe field is imaged onto a separate detector to separate the modulated scatter signals for each fringe field.

Since this multiple beam splitter concept may be expensive to manufacture, a better alternative is to image a sinusoidal absorption (or reflection) grating, with various fringe spacings, into the particle dispersion. As each particle passes through the grating image, the scattered light from that particle is modulated by the periodic intensity profile of the image. A standard optical absorption resolution target could be used to produce an image with multiple regions, each region with a different sinusoidal wavelength as shown in Figure D19, which shows a mask (or image of a mask) with four regions. The spatial frequency of each region is only for illustrative purposes. Optical systems incorporating this type of sinusoidal absorption grating (also called a line ruling) are shown in Figures D17, D18a, and D18b. Each region of the target image is imaged onto a separate detector. By using a white light source, Mie resonances are greatly reduced; but a laser source or LED may be preferred if chromatic aberration is a problem. In Figure D17, a light source, preferably a white light source, is focused by lens 1 onto a line ruling or sinusoidal target with multiple regions, each with a different fringe spacing or sinusoidal wavelength. The line ruling size is exaggerated for illustrative purposes; the light source illuminates the entire line ruling. The light

rays from the source only indicate the image planes of the source and not the beam diameters at any plane. Lens 2 images this target into the particle sample container. Lens 3 images this target image onto a set of detectors, which are positioned to capture the image of each target region onto a separate detector. The direct light from the source is blocked by a beam block which is placed behind lens 2. Only the light scattered from particles passing through the fringe image reaches the detectors.

Figure D18b shows another variation of this idea. The light source is spatially filtered through a pinhole by lenses 1 and 2, and nearly collimated through the sample container region by lens 3. Lens 3 also images the multi-region line ruling or sinusoidal grating into the sample container. Each separate region of the line or fringe pattern image has a different spatial frequency and is imaged onto a separate detector, by lens 4. The source light is blocked in the back focal plane of lens 4. Only the modulated scattered light reaches the detectors. Each detector sees the scattered light from only one spatial frequency region in the fringe pattern image, in order to separate the modulated signals.

Figure D18a shows a more compact version of this design. As in prior designs, the particles are moving through a sample cell, between two optical windows. And as each particle moves through the image of a line pattern, the scattered light from that particle is modulated by the periodic intensity distribution. The line ruling or pattern is placed in a plane which is conjugate to the region containing the particles. However, in this case the detector array is directly behind the ruling with each detector element aligned behind a different spatial frequency segment of the ruling. This configuration eliminates one lens and allows for greater demagnification of the ruling image. If lens 3 were a microscope type objective with high magnification, then the ruling and detector array could be larger, lowering the alignment tolerances of the ruling and detector array elements. At very large magnification, separate detectors could be used instead of a detector array. The beam block could also be replaced by a pinhole to measure the modulation caused by total light lost by scattering and

absorption. In both cases the higher frequency components of the signal will be similar. However in the case of the pinhole, the signal will be riding on top of a large DC offset, which must be removed by analog or electronic filtering. In size regions where Mie resonances are a problem, the pinhole may be preferred because total light lost may be less sensitive to Mie resonances.

Figures D16, D18a, and D18b show a light source followed by two lenses and a pinhole to remove unwanted portions of the source light. This subsystem could be replaced by a laser or other collimated source for illuminating the particles in the sample cell.

In figures D17, D18a, D18b, and D19, and the description above, the terms, line ruling, ruling, sinusoidal grating, sinusoidal absorption grating, and resolution target, refer to the same general object, which is a mask with periodic absorption (or reflection), with periodicity in the direction of the particle motion. The use of any one of these five terms in this document is assumed to include the other four terms. The best type of mask is one with a sinusoidal absorption pattern (see figure D19) which will produce single frequency modulation of the scattered light from particles of a single velocity. While other periodic absorption profiles (other than sinusoidal) can be used, they will produce harmonics in the scattering signal, which must be removed from the signal by deconvolution.

Each of these detector signals can be transmitted separately to the computer through multiple transmission channels. Also the signals could be sent sequentially because the spectral properties of each detector signal are stationary over short periods of time. The signal properties only change when the largest particle fraction passes through the interaction region. So a short signal segment can be sent from each detector sequentially on a single transmission channel. Also a fast A/D could do sequential multi-channel sampling where each successive sample point is from the next detector. This A/D signal is then transmitted to the computer receiver and disassembled and recombined into separate detector data streams in the computer.

For very small particles, which need short inter-fringe spacing, either the crossed laser beam (Figure D16) or heterodyne system ( figures D10-D14) should be used to obtain optimal accuracy, because the image resolution of the white light system may not produce sufficient resolution of fringe spacings below 1 micron. The crossed beam system produces high resolution fringe patterns or the heterodyne system can measure Doppler shifts at smaller particle velocities. By using the white light/sinusoidal target system for particles above approximately 1 micron and crossed-beam or heterodyne below approximately 1 micron, particles over a wide size range from 0.1 micron to greater than 1000 microns could be measured.

As mentioned before, Mie resonances may present a problem for ensemble scattering measurements because the scattering amplitude will be a multi-valued function of particle size. However in the size region between 2 and 10 microns where these resonances occur, the particle concentration could be lowered to insure that only a few particles are in the beam at any time. Low numbers of particles will produce a discrete set of line spectra in the power spectrum instead of a broad continuum, one line for each particle. These line spectra can be separated for individual counting and sizing of particles based upon their Doppler frequency. Then the variation of the amplitude of each spectral line due to Mie resonances or scattering efficiency variations will not effect the size determination. In most applications, the particle volume vs. size distribution is relative uniform and the particle count vs. size distribution is proportional to the volume distribution divided by the particle diameter cubed. So larger particles will have much lower particle number concentrations and the line spectra/counting method could be employed without coincidence problems in the line spectra. This method can count and size individual particles, with many particles in the beam at one time, provided that no two particles have the same size. Even if two particles did have the same size, the amplitude of that spectral line would be double the expected amplitude and that line could be counted as two particles. This technique is very powerful in that it allows counting and sizing of individual particles in the beam even when large numbers of particles are in the beam at one time. This method is described in more detail in another

filed application, "Methods and Apparatus for Determining the Size and Shape of Particles", filed by this inventor.

Also many of the heterodyne and fringe systems, described in "Methods and Apparatus for Determining the Size and Shape of Particles", can be placed into a centrifuge to produce the same data as described in this document.

The particle velocity detection systems in Figure D10 and Figure D15 can be replaced with the fiber optic system shown in Figures D20 and D21, using the same analysis of the power spectrum of the scatter detector current. The tip of the scatter collection optics would be immersed into the dispersion inside the particle sample container at the end closest to the rotation axis. The light beam from the scatter collection optics would be projected into the particle sample container, in a direction nearly parallel to the particle motion direction. For larger or denser particles, this system could also be used in settling mode by aligning the particle velocity axis of the sample chamber with the direction of gravitational force. The basic fiber optic interferometer is illustrated in Figure D20. A light source is focused into port 1 of a fiber optic coupler. This source light is transferred to port 4 and light scattering optics which project the light into the particle dispersion and collect light scattered from the particles. This scattered light is transferred back through the fiber optic and coupler to the detector on port 2. If the coupler has a third port, a portion of the source light also continues on to port 3 which may provide a local oscillator with a reflective layer. If the local oscillator is not provided at port 3, a beam dump or anti-reflective layer may be placed onto port 3 to eliminate the reflection which may produce interferometric noise in the fiber optic interferometer. The beam dump could consist of a thick window which is attached to the tip of the fiber with transparent adhesive whose refractive index nearly matches that of the fiber and the window. This will reduce the amount of light which is Fresnel reflected back into the fiber at the fiber tip. The other surface of the window can be anti-reflection coated, and/or be sufficiently far (thick window) from the fiber tip, so that no light, which is reflected from that surface, can enter the fiber. The details of the scatter



collection optics are shown in Figure D21. A GRIN rod or conventional lens is used to project the source light into the dispersion. The projected beam can be weakly focused, or nearly collimated, to provide nearly equal contribution of scatter from particles throughout an extended region of the sample container, as shown in figure D22. In this way, the heterodyne signals from a large group of scatters could be measured for a long period, which ends when the highest velocity particles leave the region where scatter can be detected. After the larger particles have left that region, the centrifuge can be stopped (or the sample cell could be turned to be perpendicular to the settling direction) and then the Brownian motion of the remaining smaller particles could be measured, with the same heterodyne system, to determine the size distribution of particles which are too small to have sufficient terminal velocity to be measured under the centrifugal force or settling. The beam could also be strongly focused, as long as the larger particles remain in the scatter interaction volume for sufficient time to gather the Doppler shifted signals. As before, after the larger particles leave the interaction volume via settling or centrifugal force, the remaining smaller particles can be measured by measuring the dynamic light scattering due to Brownian motion of the remaining particles.

The fiber optic system and electronics would be mounted into the center portion of the rotor to minimize the centrifugal force on the fiber components. And the scatter signals would be transmitted to the stationary computer by any of the methods described above, including optical coupling and radio transmission.

The scattering efficiency for large particles is much higher and less multi-valued at lower scattering angles. Therefore, to detect the larger particles in settling and centrifugal mode, or Brownian motion mode, additional detectors are required to measure scattered light at lower scattering angles as shown in figure D22. Figure D22 shows system A, which projects light into the sample cell and collects scattered light at approximately 180 degrees along with the local oscillator which is Fresnel reflected from the exit surface of the scatter collection optics A, as described previously. A second optical system B is

connected to port 3A of system A to provide local oscillator to be mixed with scattered light from scatter collection optics B, which collect scattered light at lower scattering angles. The length of the fiber optic loop is chosen to match the optical pathlengths from the source through port 3B to detector B with the total optical path through port 4A and port 4B to detector B. In this way Detector A collects high angle scatter and Detector B collects low angle scatter. Both detectors operate in heterodyne mode using the light from a single source. Scatter collection optics B collects scattered light through a coupling prism which is attached to the window of the sample cell with index matching adhesive to reduce Fresnel reflections at that interface. Both detectors will see dynamic scattering which includes both a Brownian motion component and centrifugal or settling component in the power spectrum of the detector current. Essentially, the power spectrum is a symmetrical function, whose spectral width is determined by spectral broadening caused by Brownian motion. The center of this symmetrical function is shifted to the Doppler frequency due to settling or centrifugal induced motion of the particles. So for very small particles, the spectrum will be very broad, with the center of the function close to zero frequency. For large particles, the spectrum will be narrow with a large shift from zero frequency. These two effects are included in the matrix equation which is used to model this power spectrum, as shown previously. This model is then inverted to determine the particle size distribution from the measured power spectrum, as described previously. Better size distribution accuracy is obtained by measuring the power spectrum under two different conditions, using the appropriate model for each condition, and then combining particle size results from inverting these two models separately or by combining both model's matrices into one single matrix and solving that larger linear system. The first condition is with particles under centrifugal or gravitational force along the direction, which provides maximum Doppler shift for the low angle scattering detector, nearly parallel to the angular bisector between the forward scatter direction and the light beam in the sample cell. The second condition is in the absence of the centrifugal force or with the gravitational force nearly perpendicular to the angular bisector between the forward scatter direction and the light beam in the sample cell. At this

angle the Doppler shift due to gravitation will be minimized. If the most important size information is contained in the backscatter direction, then the two cases should be with alignment of the gravitational or centrifugal force in directions parallel to, and then perpendicular to the light beam (instead of the bisector mentioned previously). Another useful data separation is to measure the Brownian motion of the smaller particles after the larger particles have been removed from the dispersant due to settling or centrifugal force, so as to remove the background signal fluctuations caused by the larger particles. Also power spectrum measurements can be made at various times during the settling or centrifugation process to measure different size fractions of the sample as described previously in this document. In this case a focused light beam may be more appropriate to provide a smaller interaction volume, which larger particles can leave more quickly, providing faster separation of different size fractions.

Many of the scattering detection systems, described in the application "Methods and Apparatus for Determining the Size and Shape of Particles" by this inventor, can also be employed as the detection means in the systems described in this document.

Many figures in this document contain optical rays which are drawn only to define object planes, image planes, and focal planes. The numerical apertures, beam diameters, and lens diameters are not necessarily drawn to scale.